Reduced Precious Metal Catalysts for Methane and NOx Emission Control of Natural Gas Vehicles

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ACE128

Overview

Timeline

- Start: May 1, 2018
- End: April 30, 2021
- 60% complete

Barriers/Targets

- Methane is greenhouse gas (25x CO_2); CH_4 GHG emissions above the 30 mg/mi light- duty vehicle cap count against fuel economy
- U.S. EPA mandates tailpipe methane emissions at 0.1 g/bhp-h for heavy-duty vehicles (95% reduction) & NOx emissions at 0.2 g/bhp-h
- State-of-art three-way catalyst (TWC) ineffective for methane oxidation at < 400 ^oC

Need for low cost emission catalyst for stoichiometric NG vehicles

Budget

R1

- Total project funding:
  - DOE: $1,640k (excl. ORNL)
  - UH & partners: $525k
- 3/31/2020 expenditure update:
  - $837k federal (excl. ORNL)
  - $397k cost share

Partners

- U. Houston (lead)
- CDTi Advanced Materials, Inc.
- University of Virginia
- Oak Ridge National Lab

Key Acronyms

- NGV: natural gas vehicle
- FWC: four-way catalyst
- PGM: Platinum group metal
- HC: hydrocarbon
- NOx: NO + NO_2
- OSM: oxygen storage material
- DOSC: dynamic oxygen storage capacity
- DFT: density functional theory
- SpaciMS: spatially-resolved mass spectrometry

Reviewer Comments from 2019 AMR

- **Technical Barriers (TB)**

  TB1: The reviewer was interested to see the mechanistic conclusions regarding the influence of the spinel on performance during modulation (and why modulation can be tuned).

- **Technical Accomplishments (TA)**

  TA1: The reviewer noted that DFT studies are helping to discover and assess new materials, although it is not clear how well these are integrated with the flow-reactor studies and if there is a rapid screening process in place for new materials.

  TA2: The team has been able to get 50% methane conversion at 350°C and 10% at 300°C, which are promising but not yet at the target.

- **Collaboration (C)**

  C1: The combination of the DFT approach and flow reactor was not apparent to the reviewer, who inquired as to how many new materials were discovered through DFT and how many of those were tested through flow reactor studies. The reviewer noted that it will be good to see a scatter plot showing light-off temperatures on the flow reactor versus a DFT-based metric for various materials.

Reviewer Comments from 2019 AMR

- **Proposed Future Research (PFR)**

  PFR1: The reviewer remarked that the project team is proposing a lot of future work (Tasks 2.1 through 2.9 in the presentation), which seems very ambitious for the next year or two. The reviewer agreed that those tasks are necessary, especially to improve methane conversion below 300°C. According to the reviewer, it would be good to understand how spinel enhances the methane conversion, especially when cycling around stoichiometric conditions.

  PFR2: Sulfur tolerance is in scope, not done yet, and it was encouraging to the reviewer to see this being done sooner rather than later as it is better to find out early if the material has serious degradation issues with sulfur. Also, the reviewer suggested that some hydrothermal aging should be included to assess end-of-life performance of the catalysts. Also, the reviewer stated that it will be good to include more spinel compositions in the study (the reviewer was not clear if the chosen one is optimum). This will be especially important and useful to further reduce the light-off temperature.

- **Relevance (REL)**

  n/a

- **Resources (RES)**

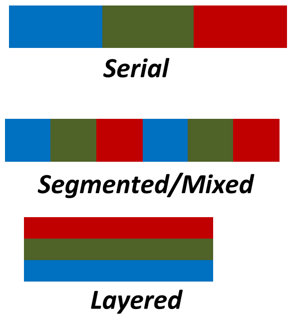
  R1: It looked to the reviewer like the total budget is $2.5 million over 3 years (or roughly $800,000 per year), which seems generous, especially since the year 1 budget was $660,000. The reviewer wanted to know how the money will be spent and if there are more resources coming available to support the ambitious set of future tasks.

Relevance: Project Premise and Hypothesis

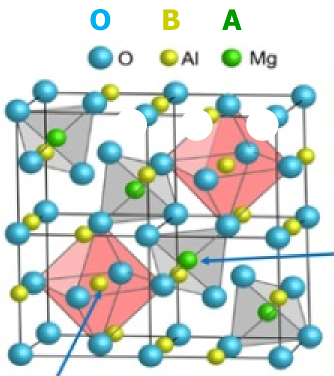
Develop the: ***FWC = Four Way Catalyst***

to enable reduced emissions of CH_4 in addition to CO, NOx & NMHCs from CNG-fueled vehicles

Material	**OSM**	+	**OXYCAT**	+	**N-RC**	**? =**
	AB_2O_4 /Al_2O_3		Pt/Pd /Al_2O_3		Pt/Rh/Al_2O_3	
Function(s)	**O2 storage & release**		**CH4 + HC + CO oxidation**		**NO_x reduction**	



Spinel in combination with low levels of precious metals are cost-effective solution for coupled methane, CO and NO_x conversion in stoichiometric natural gas vehicle exhaust.

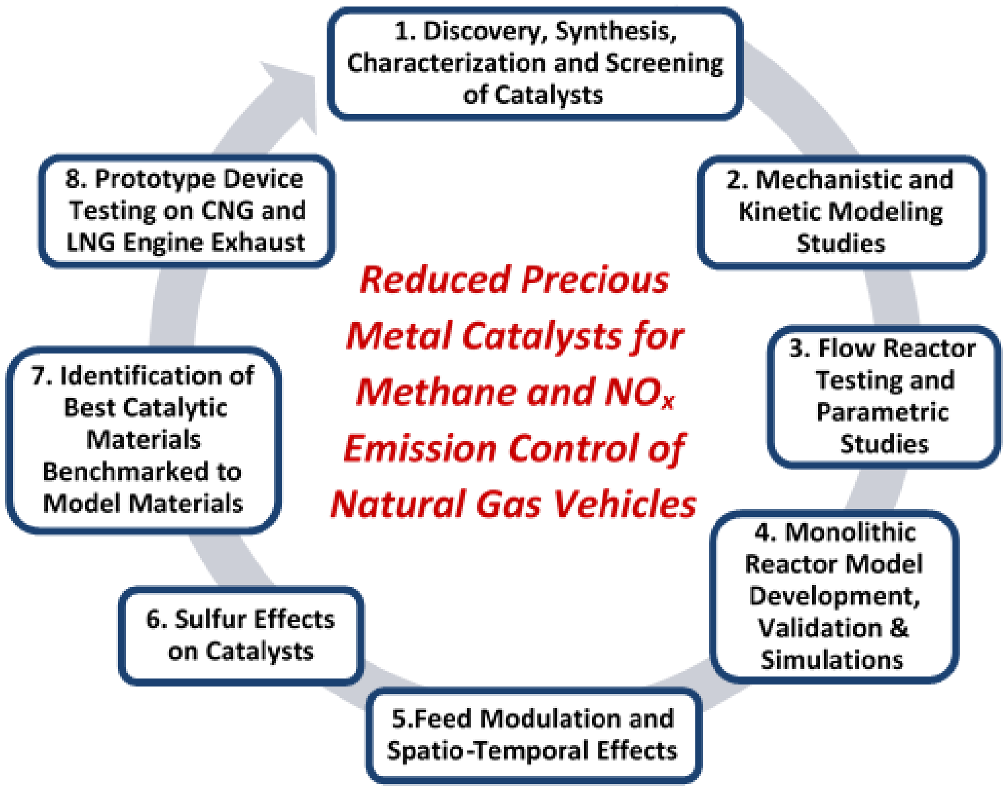


A Site – one metal with 4 nearest-neighbor O's **Tetrahedral Site**

B Site – one metal with 6 nearest-neighbor O's **Octahedral Site**

Spinel AB_2O_4

Project Approach and Collaborations



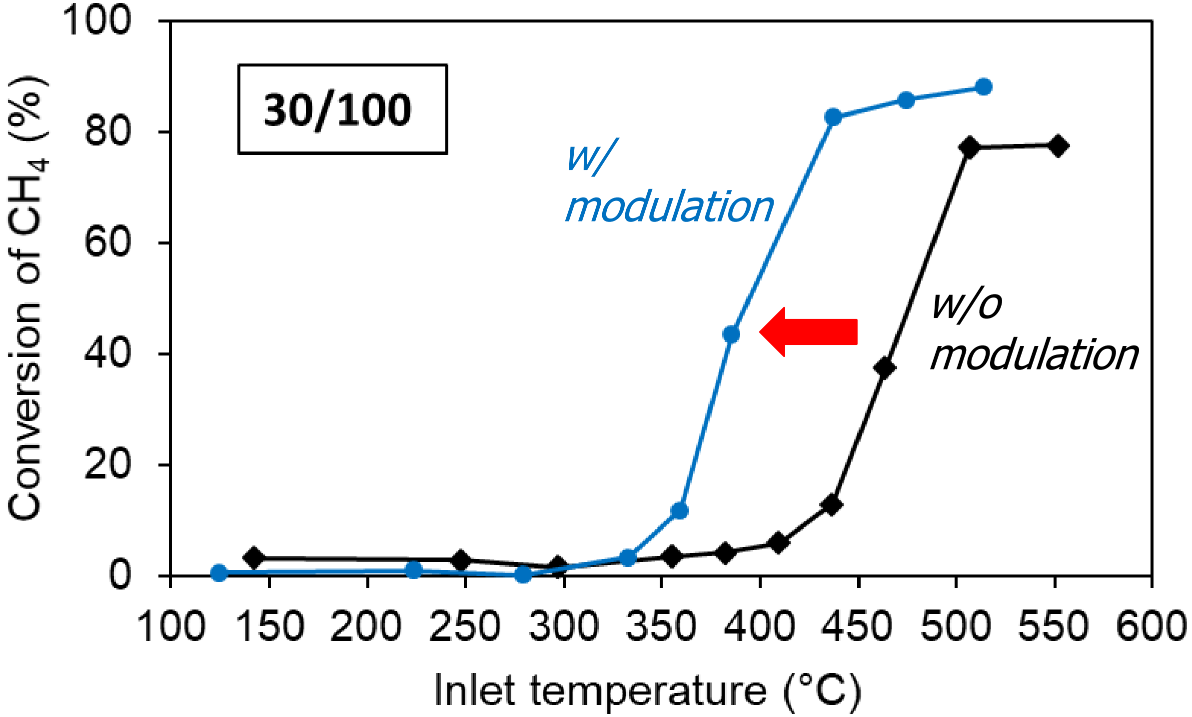
Comprehensive program spanning discovery, development, evaluation, and technology transfer will help to bring down cost barriers and accelerate the deployment of NGVs in the medium- and heavy-duty sectors

Lower Light-off Temperature with Modulation

Modulation of lean-rich ratio increases apparent catalytic activity for methane oxidation

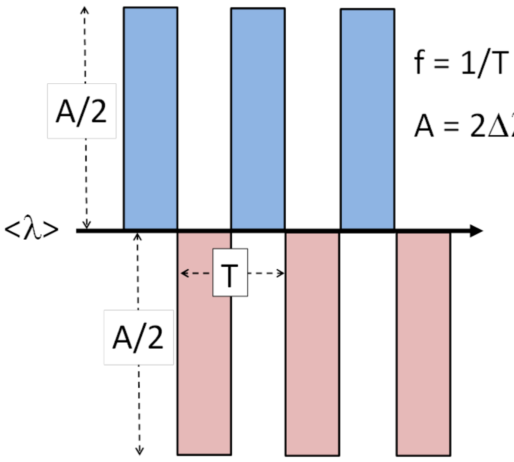
PGM/S: (g PGM/ft^3)/(g Spinel/L)

Spinel: $Mn_{0.5}Fe_{2.5}O_4$



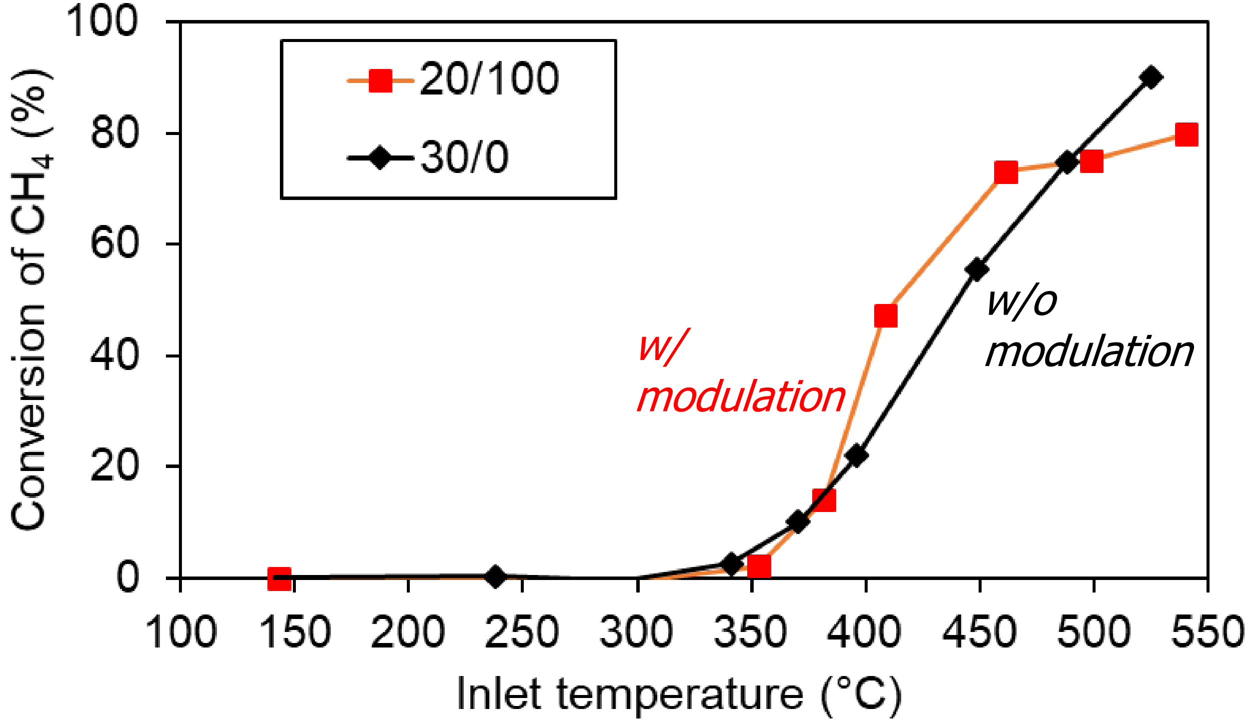
GHSV =40 hr^{-1}
<λ> = 0.992
f = 0, 0.33 Hz
A = 0, 0.028

Modulation decreases light-off temperature by ~100 ^{o}C



Reduced PGM Loading with Modulation

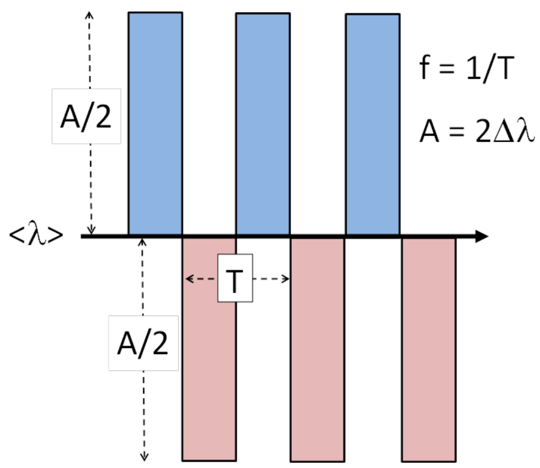
PGM/S: (g PGM/ft³)/(g Spinel/L)



Spinel: $Mn_{0.5}Fe_{2.5}O_4$

GHSV =40 hr⁻¹
<λ> = 0.992
f = 0, 0.33 Hz
A = 0, 0.028

Modulation reduces PGM loading by 10 g/ft³



BP2 Milestones

Milestone	Type	Description	Update
Additional Materials Discovery Complete	Technical	Identify at least three additional FWC materials from descriptor-based DFT.	Large number of spinels have been rank-ordered in terms of two descriptors pertaining to methane oxidation activity and oxygen storage capacity.
Materials Synthesis and Screening Complete	Technical	Synthesize and screen performance of materials identified in Task 2.1.	Screening of spinels continues with several candidates identified containing Co, Ni, Mn, and Fe. Experiments underway to quantify dynamic O_2 storage and release of spinels and methane oxidation kinetics.
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Rank-Ordering of All Tested Materials Complete	Technical	Rank-order all tested FWC materials in terms of performance with USDRIVE protocol feed.	Database continues to be populated with spinel powders and PGM+spinel monoliths with regards to activity and oxygen storage capacity.
Identification of Candidate Material Complete	Go/No Go	Develop and demonstrate predictive model that predicts performance of Baseline FWC within 15% and which can be used for optimization.	Model framework developed with kinetics studies underway to provide predictive methane oxidation and O_2 storage/release.

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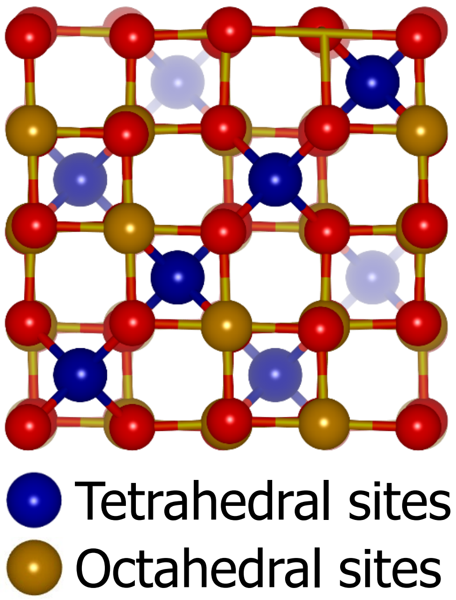
DFT Descriptors for CH_4 Conversion



Oxygen vacancy formation energy

- indicates lattice oxygen release/uptake

H-binding energy

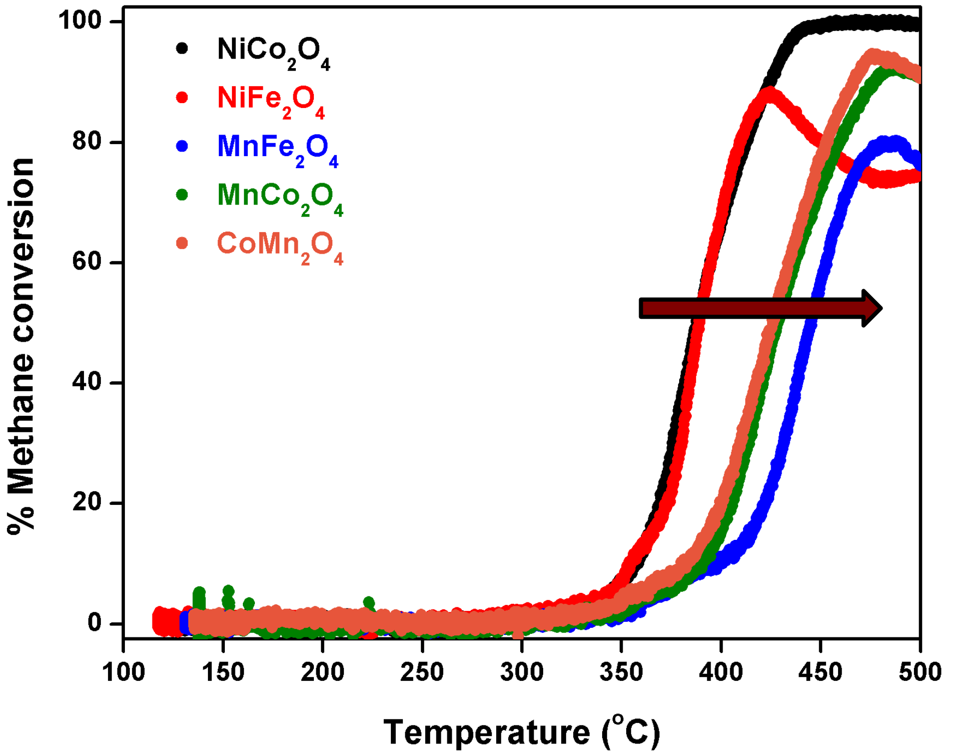
- indicates C-H bond activation (a key step for hydrocarbon oxidation)

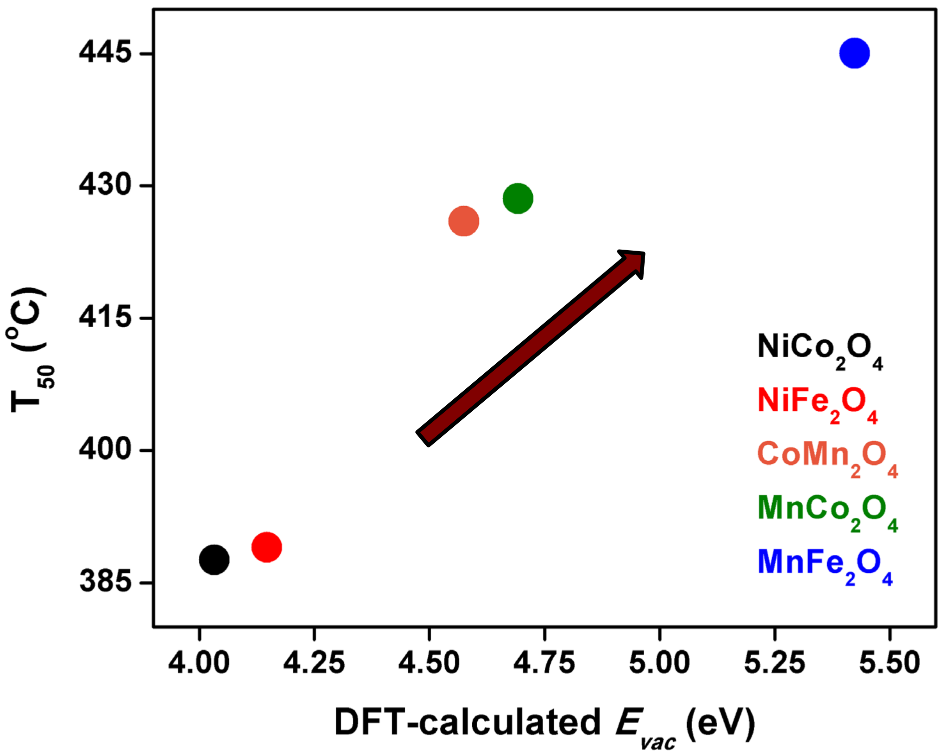
Both descriptors closely related to structure and composition of the Spinels, and can be used for performance screening

Structure - composition space of spinel oxides ($A_{1+x}B_{2-x}O_4$)

- Structural Phases: Normal; Semi-Inverse; Inverse
- Compositions: A, B = {Mn, Fe, Co, Ni}

CH_4 Conversion Performance of PGM/Spinels



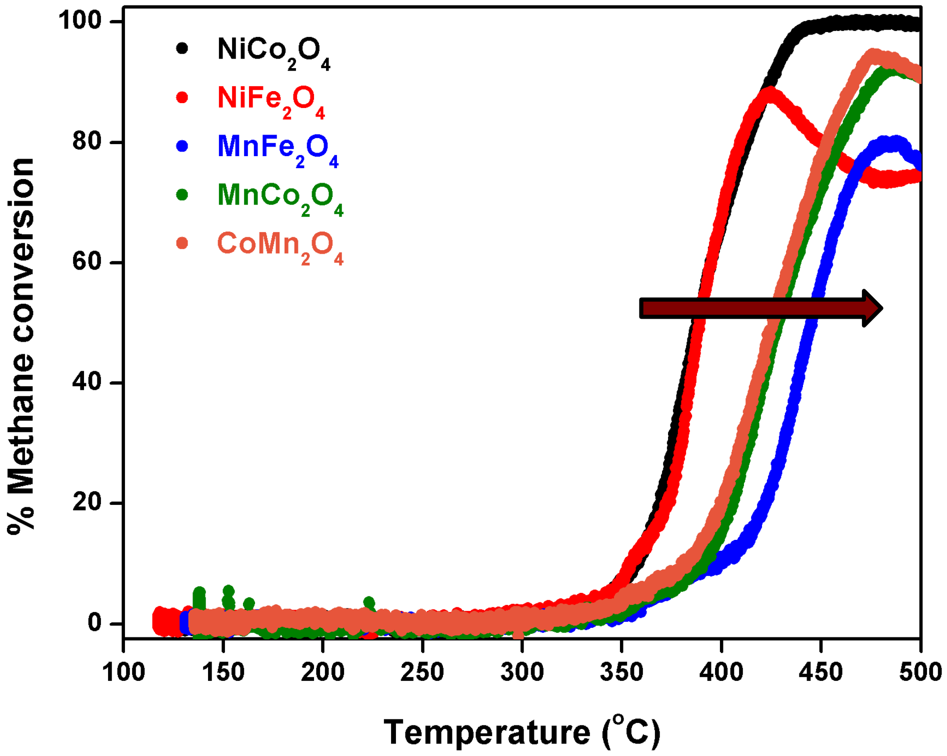


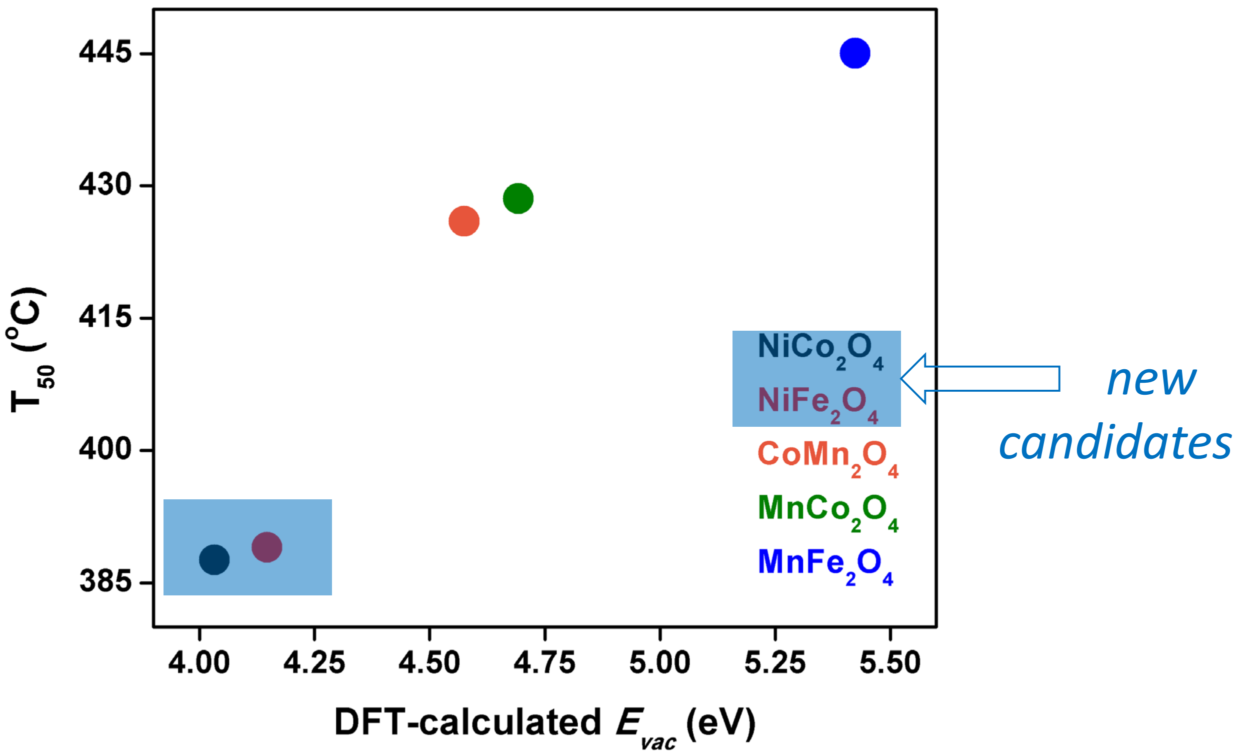
C1

Steady-state feed over PGM/spinel (10 wt% spinel/alumina), avg. λ = 0.92, 10 °C/min ramp rate

Methane conversion activity (T_{50}) directly correlates with DFT-calculated oxygen vacancy formation energy trends

CH_4 Conversion Performance of PGM/Spinels





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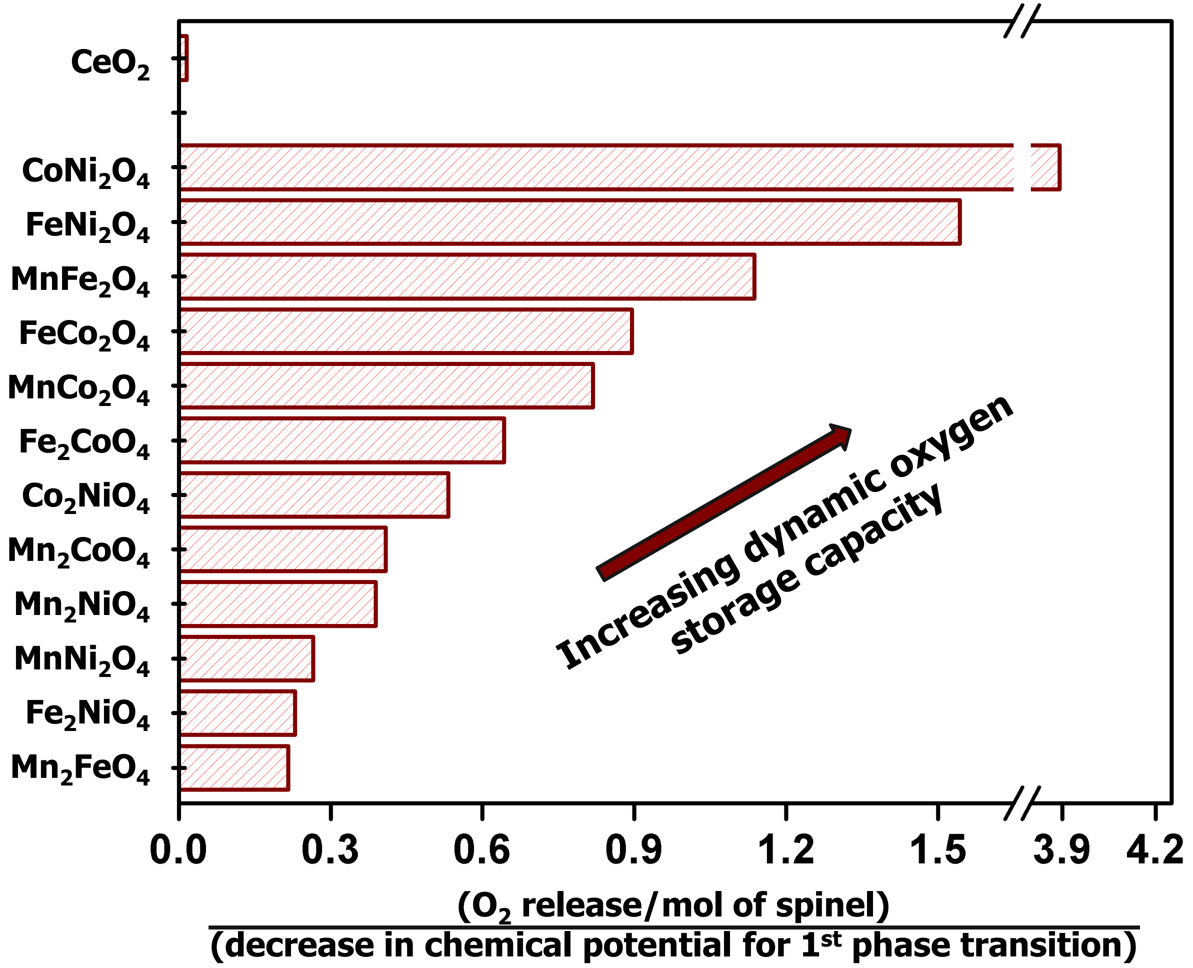
DOSC-based Rank Ordering of Spinels



TA1

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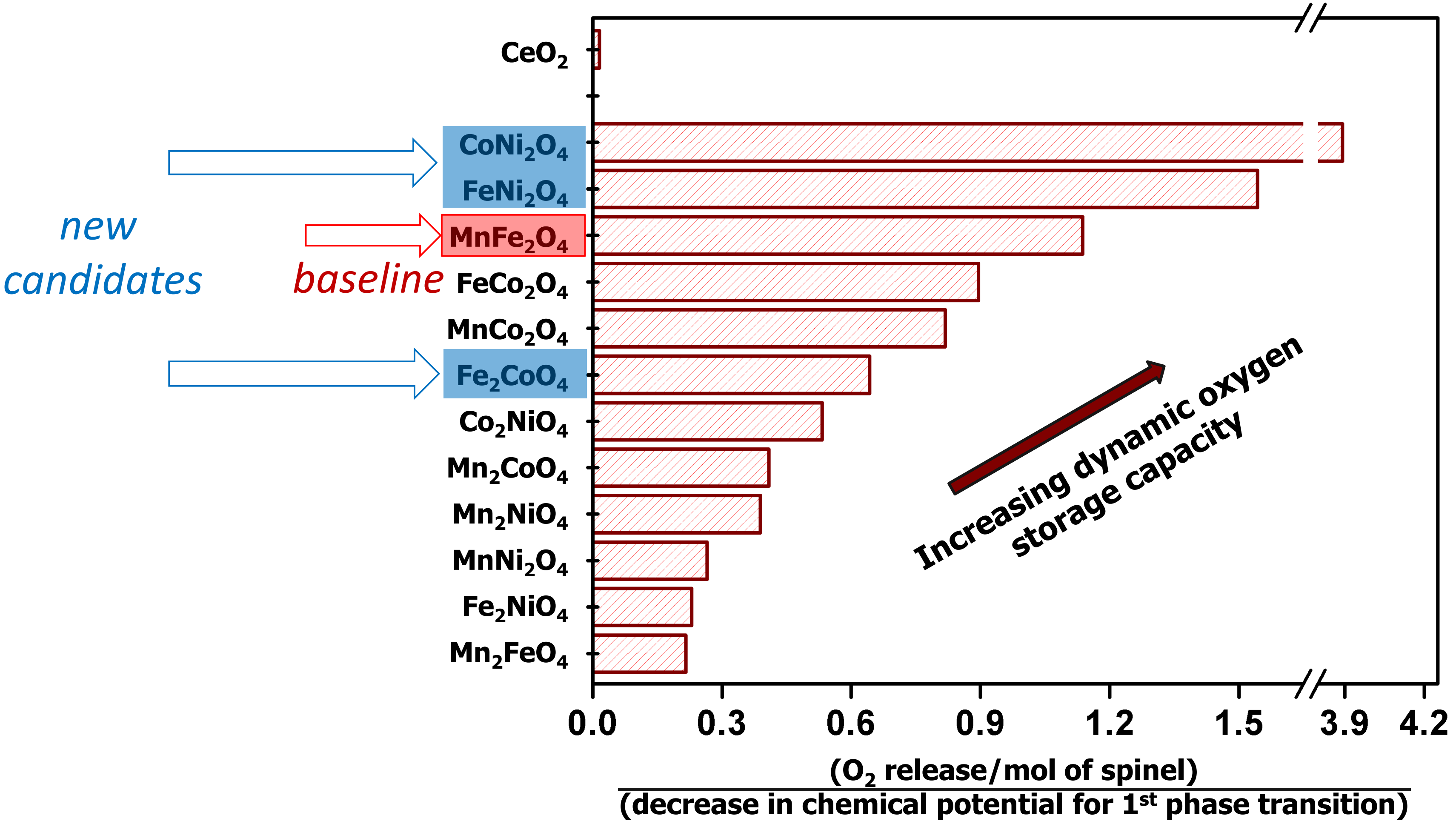

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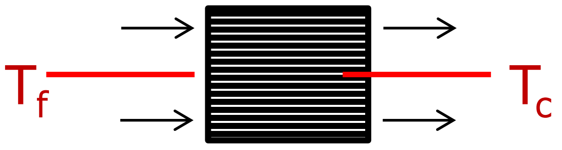
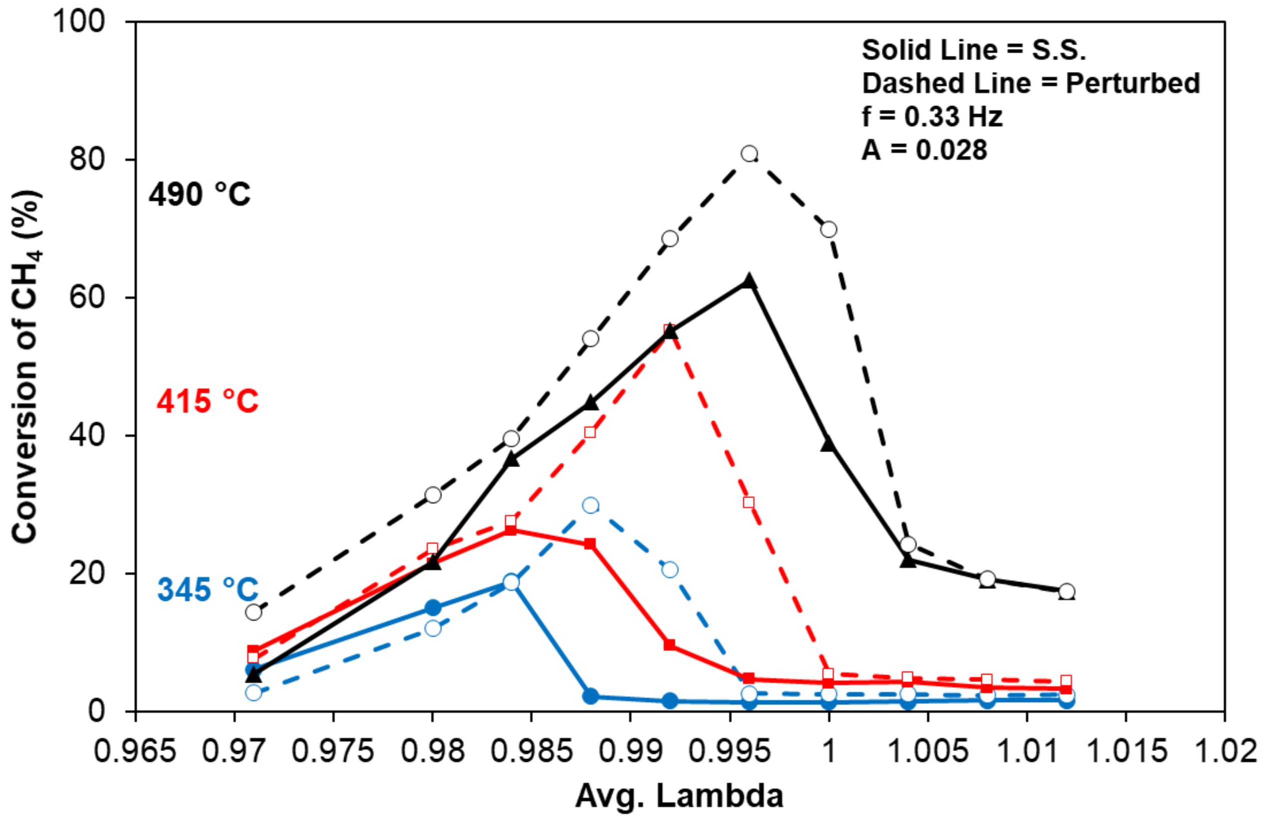
Lambda Sweep: Impact of Modulation

Steady-state Feed (20 min. at fixed inlet temp.)	Full Feed w/o modulation	Full Feed w/ modulation
	λ= 0.984 – 1.007	<λ> = 0.984 – 1.007 @ 0.33 - 1 Hz
CH_4	1500 ppm	1500 ppm
CO	8000 ppm	8000 ppm
H_2	1000 - 2000 ppm	1000 – 2000 ppm
NO	1000 ppm	1000 ppm
O_2	fixed	variable



Monolith Catalyst
(1 x 0.84 in.)

(30 g PGM/ft^3; 100 g S/L) PGM + Spinel Catalyst (30/100)
Without vs. With modulation



$$\lambda = \frac{0.5 \times [CO + 2{*}O_2 + NO + H_2O + 2{*}CO_2]}{[CO + CH_4 + CO_2] + 0.25 \times [2{*}H_2 + 4{*}CH_4 + 2{*}H_2O]}$$

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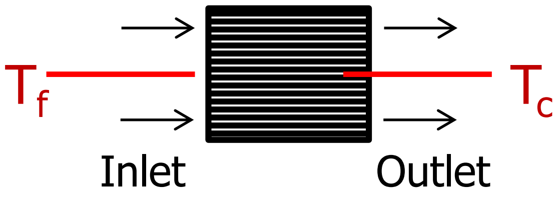

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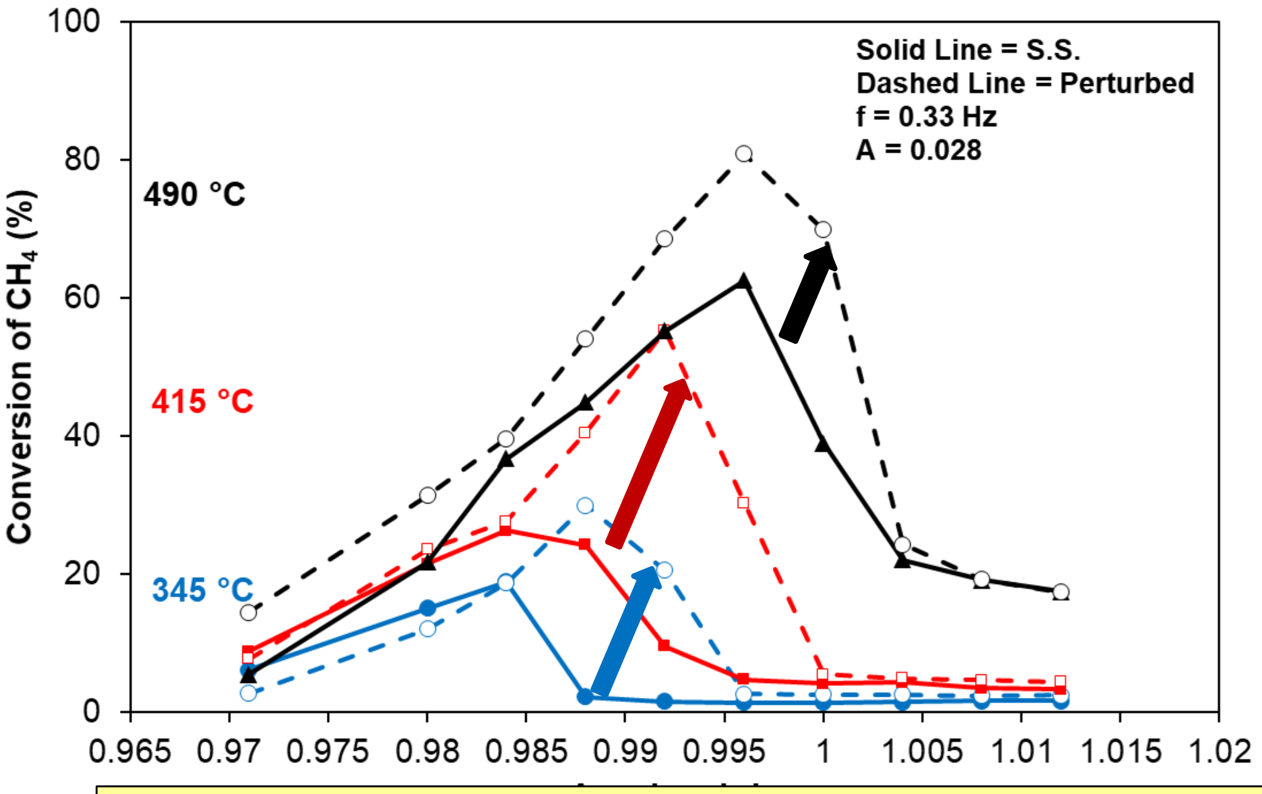


- *Modulation increases conversion*
- *Modulation moves peak towards to λ = 1*

Impact of Sulfur

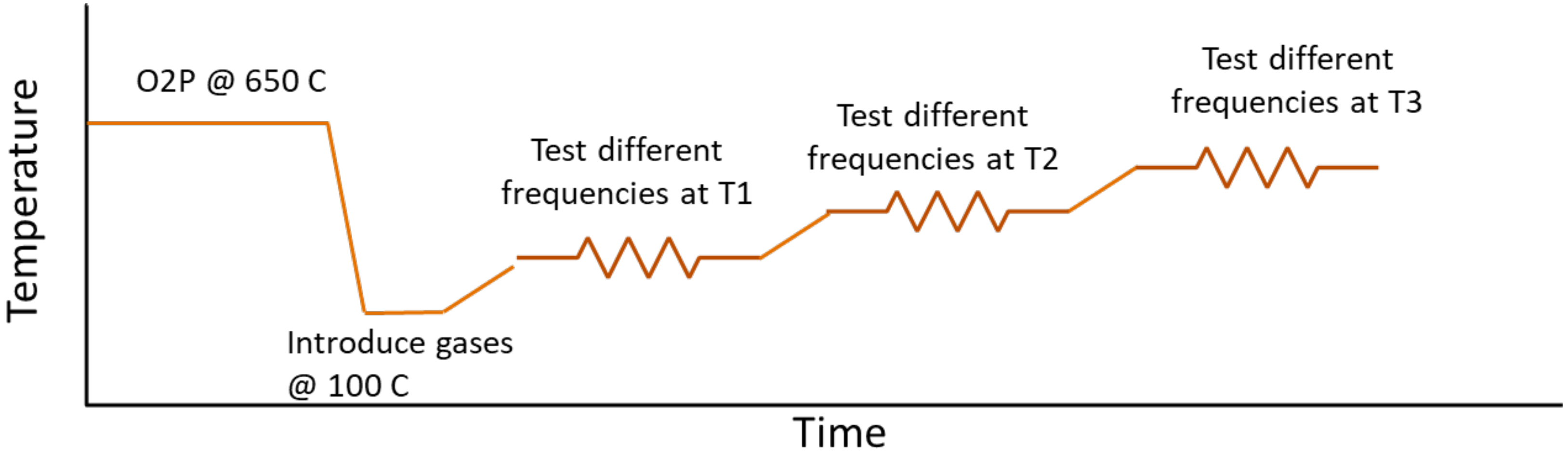
Species	Concentration
CH_4	4000 ppm
CO	4500 ppm
NO	500 ppm
H_2O	18.5%
CO_2	9.5%
H_2	1500 ppm
SO_2	15 ppm

A	$\langle\lambda\rangle = 1$; λ range	$\langle O_2 \rangle$ (%)
0.10	0.95 - 1.05	1.12
0.06	0.97 - 1.03	1.12
0.02	0.99 - 1.01	1.12

Evaluate effect of added SO_2 on modulated reactor performance

PFR2

Flowrate (L/min)	1 L/min
GHSV (hr^{-1})	60,000
Temperatures (C)	400, 450, 500, 550
Frequencies (Hz)	1, 0.5, 0.333, 0.25, 0.2



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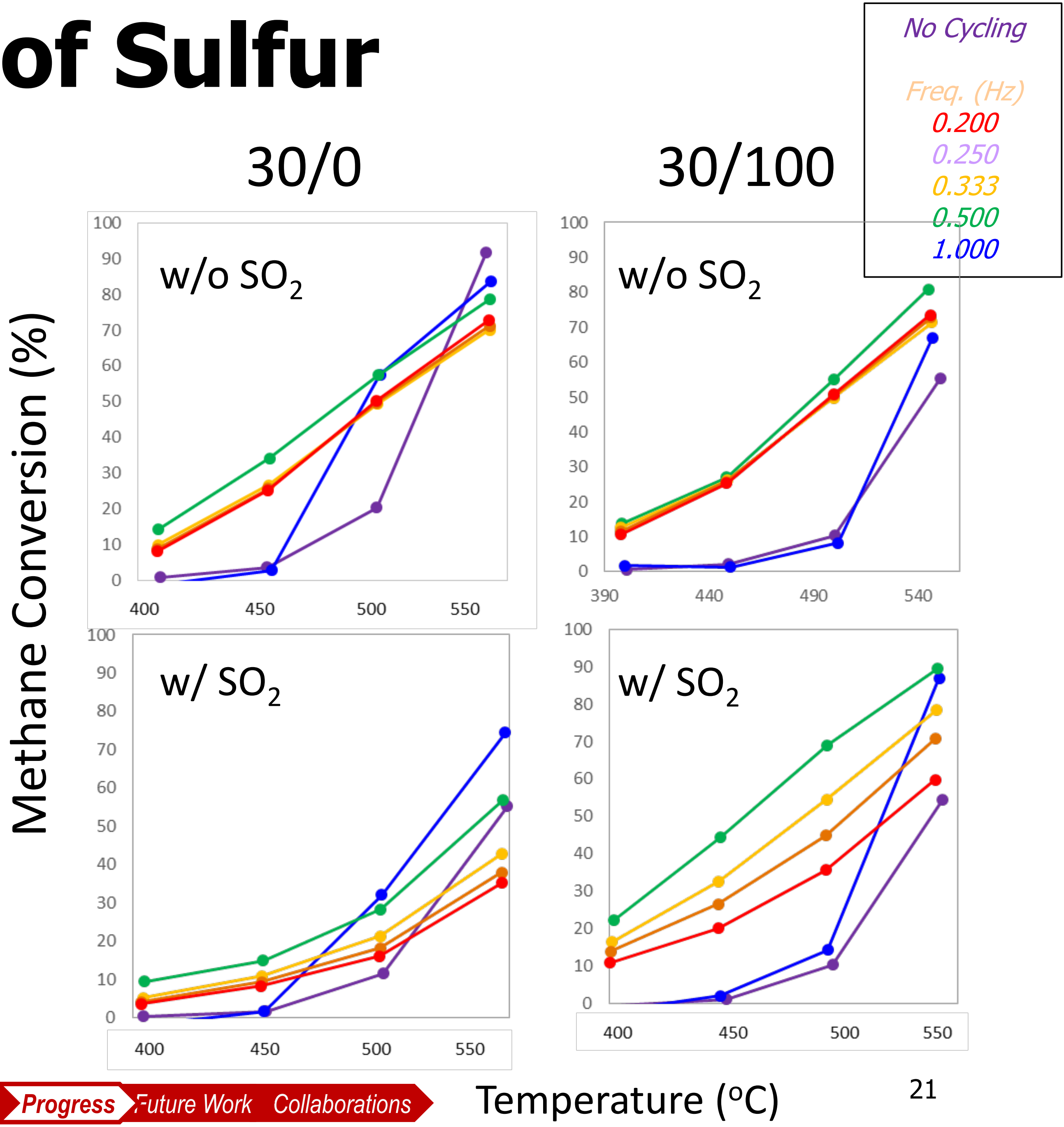

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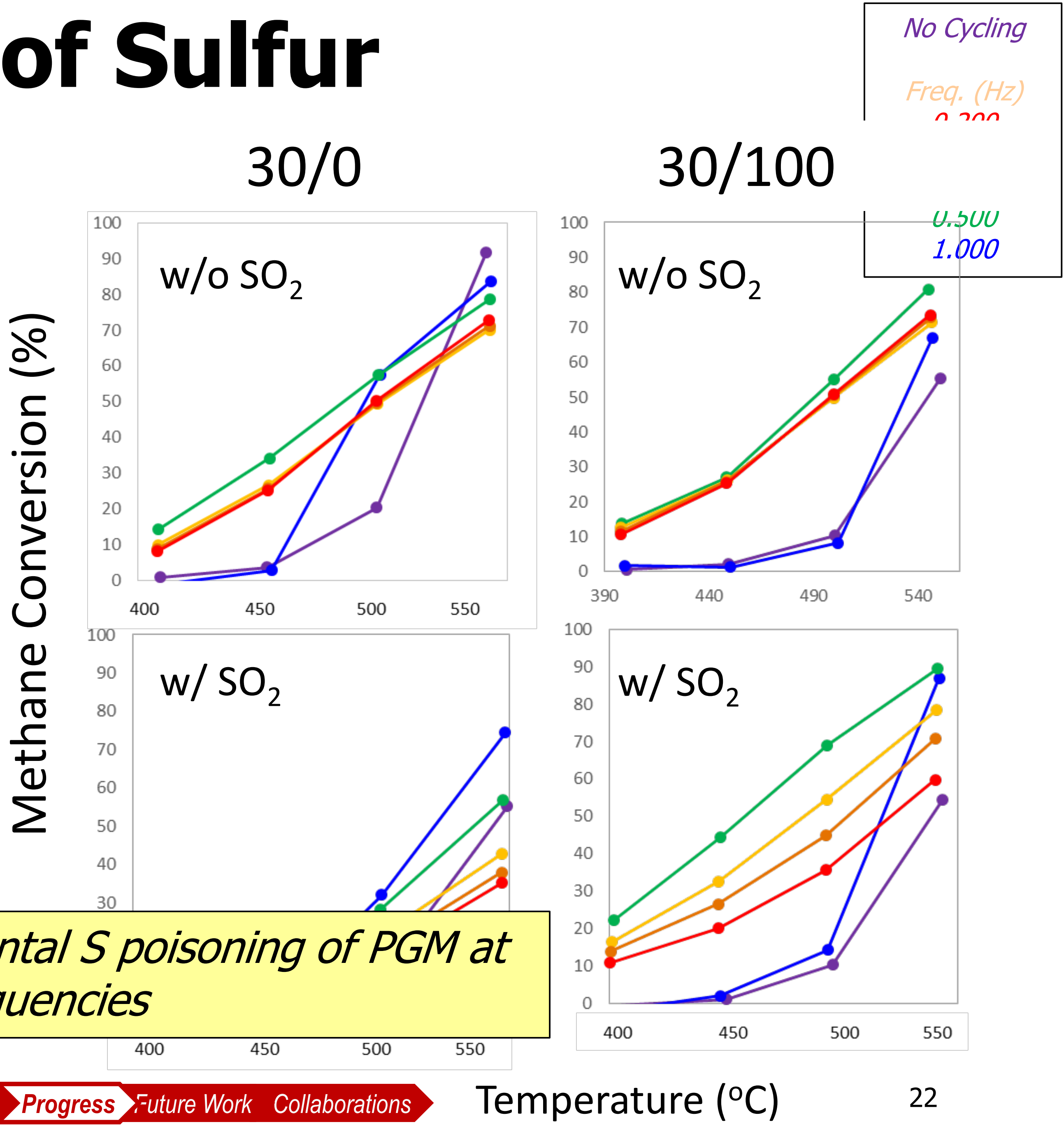

Spinel mitigates detrimental S poisoning of PGM at selected modulation frequencies

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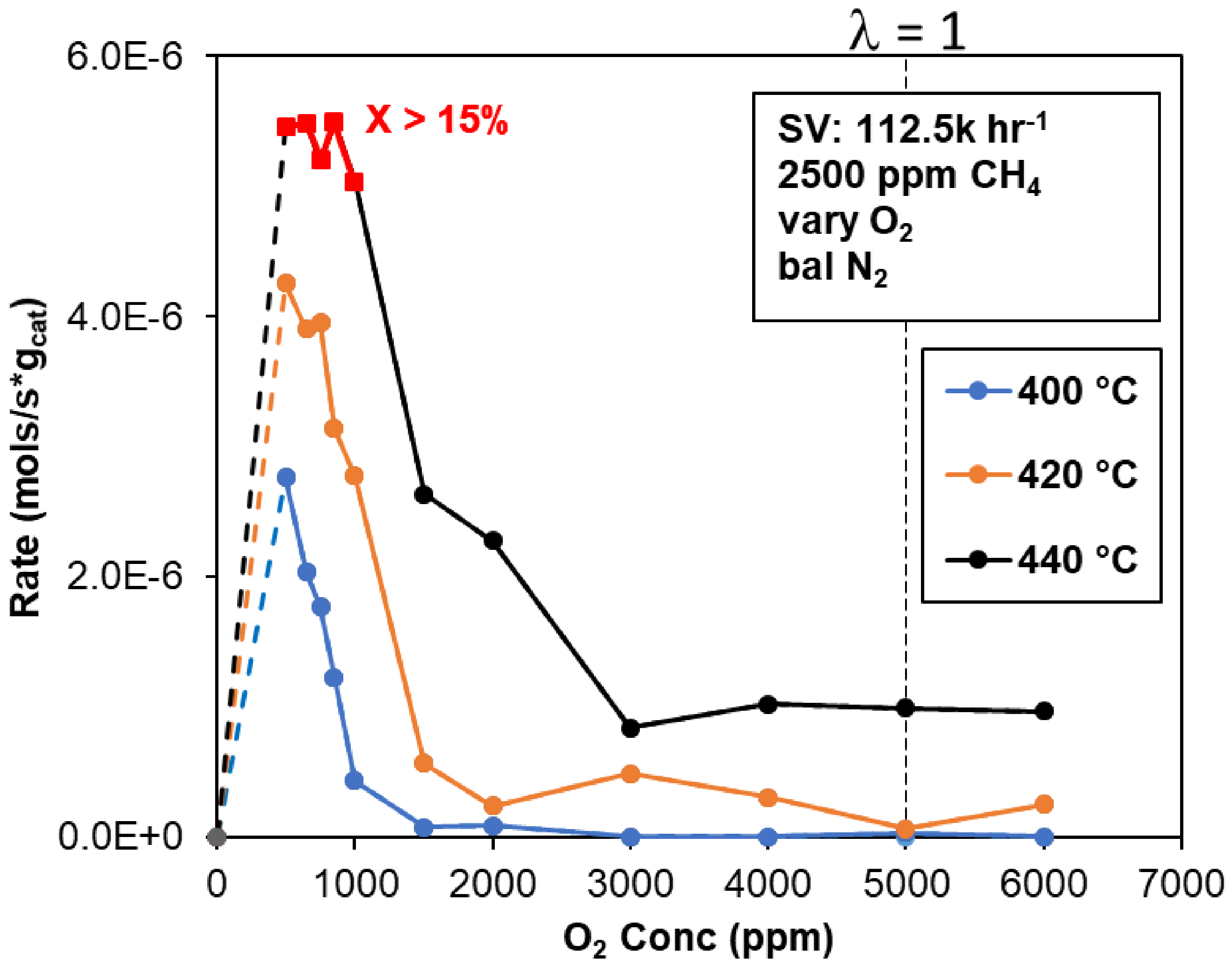
Modulation Enhancement Mechanism: Methane Oxidation Kinetics

$O_2 + Pt + Pt \rightarrow O\text{-}Pt + O\text{-}Pt$
$CH_4 + Pt + O\text{-}Pt \rightarrow CH_3\text{-}Pt + OH\text{-}Pt$
$CH_3\text{-}Pt + n(O\text{-}Pt) \rightarrow CO + H_2 + (n+1)Pt$

Partially oxidized Pt is key to activating CH_4



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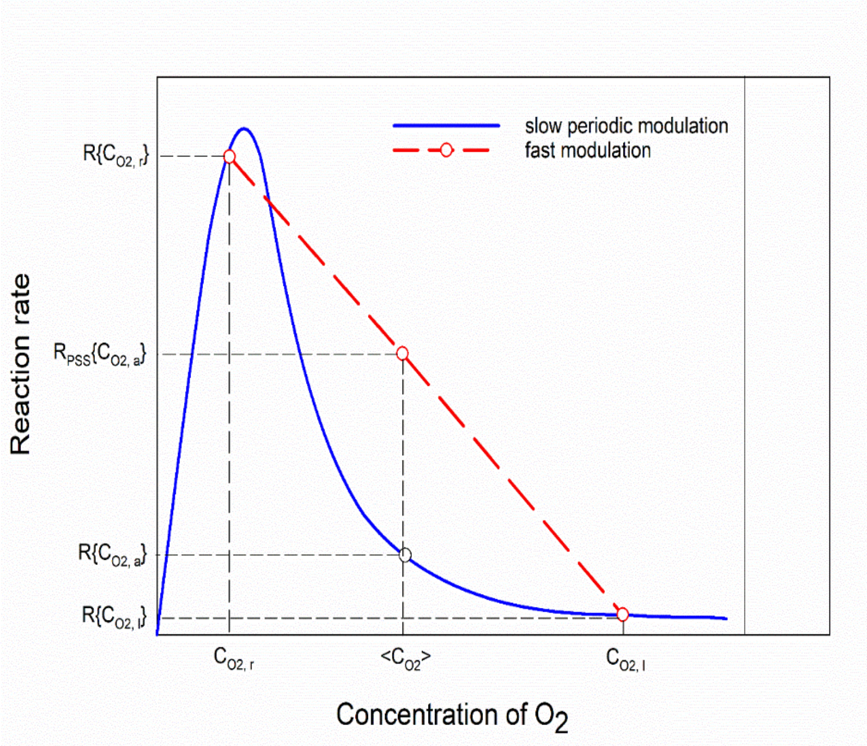
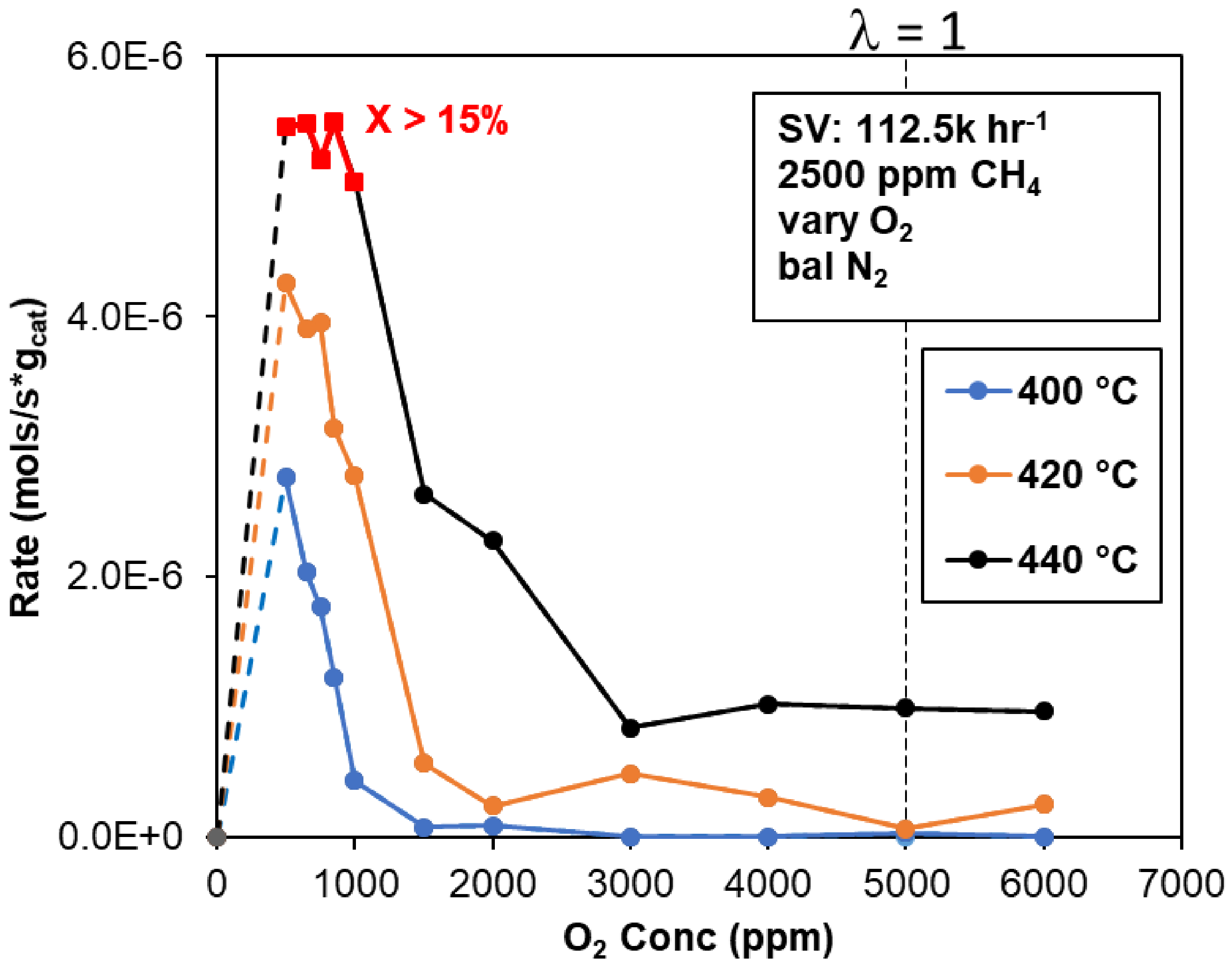
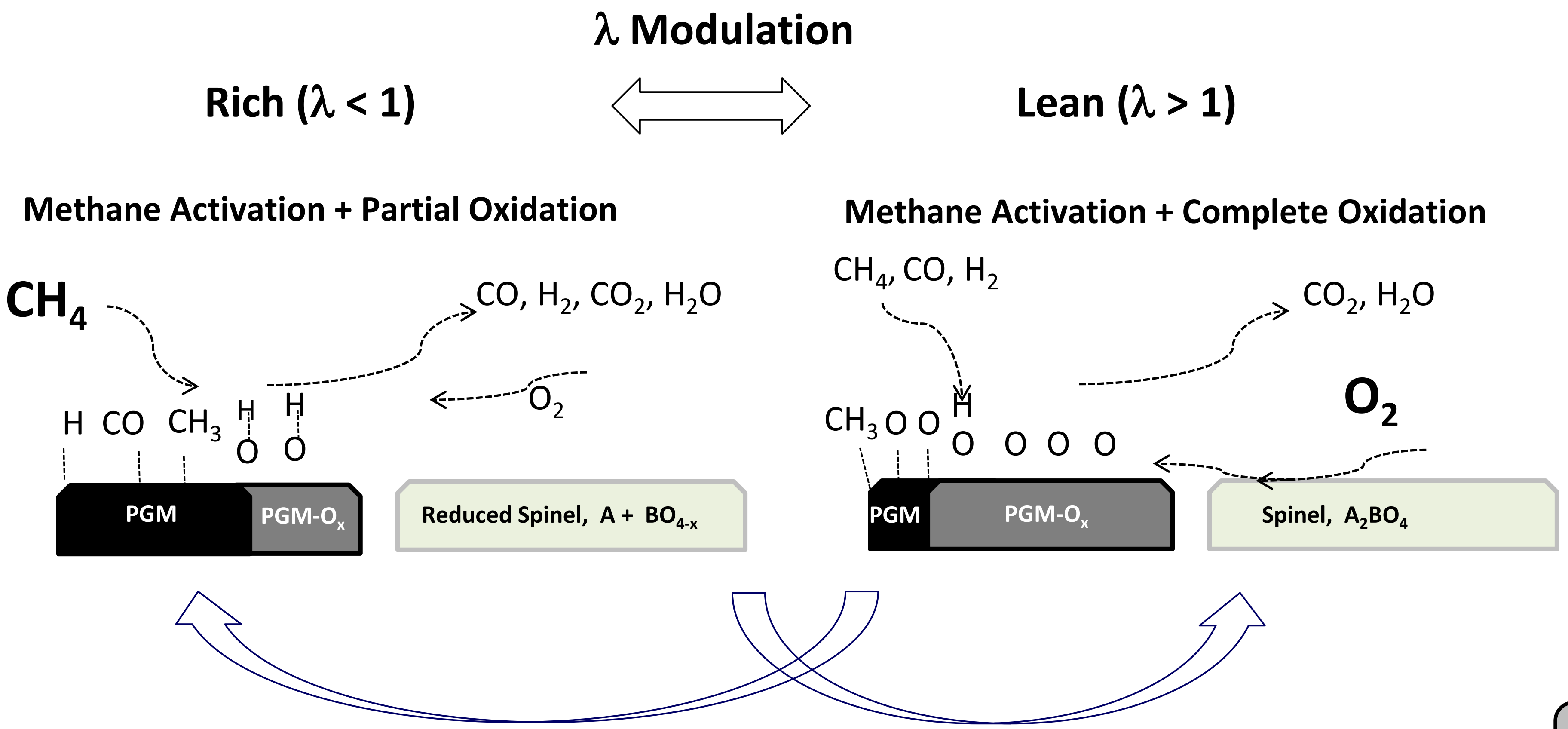


- *Slow modulation → steady state*
- *Fast modulation → unsteady steady state*



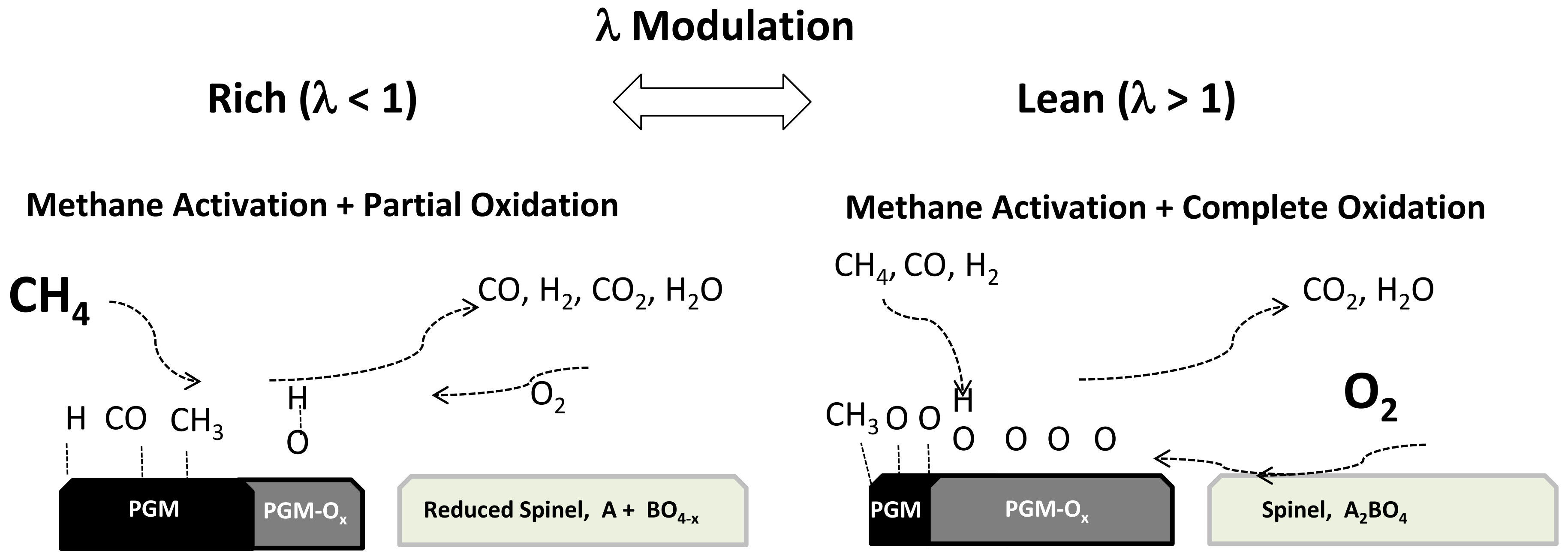
Conversion Enhancement Mechanism



TB1

PFR1

Conversion Enhancement: Proposed Mechanism



TB1

PFR1

*Key roles of **modulation** & **spinel addition** are to achieve a more favorable partially oxidized PGM at a λ value closer to stoichiometric: net result is a higher methane conversion and lower NH_3 selectivity*

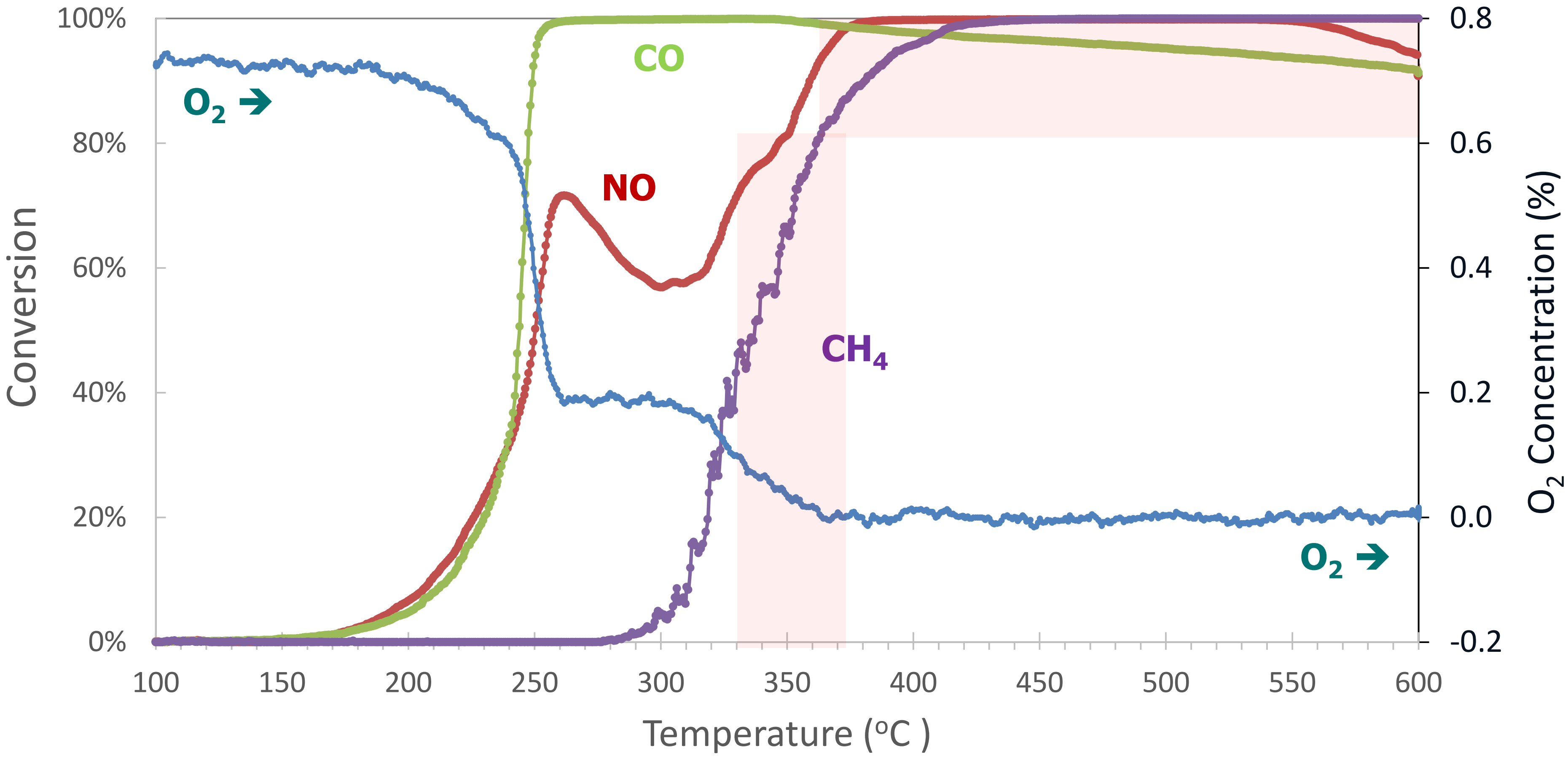
CH_4 Conversion Light-off: $NiCo_2O_4/Al_2O_3$ + Pt+Pd/Al_2O_3 Dual Layer

Pt/Pd 30g/ft³ in Alumina

NiCo2/Alumina

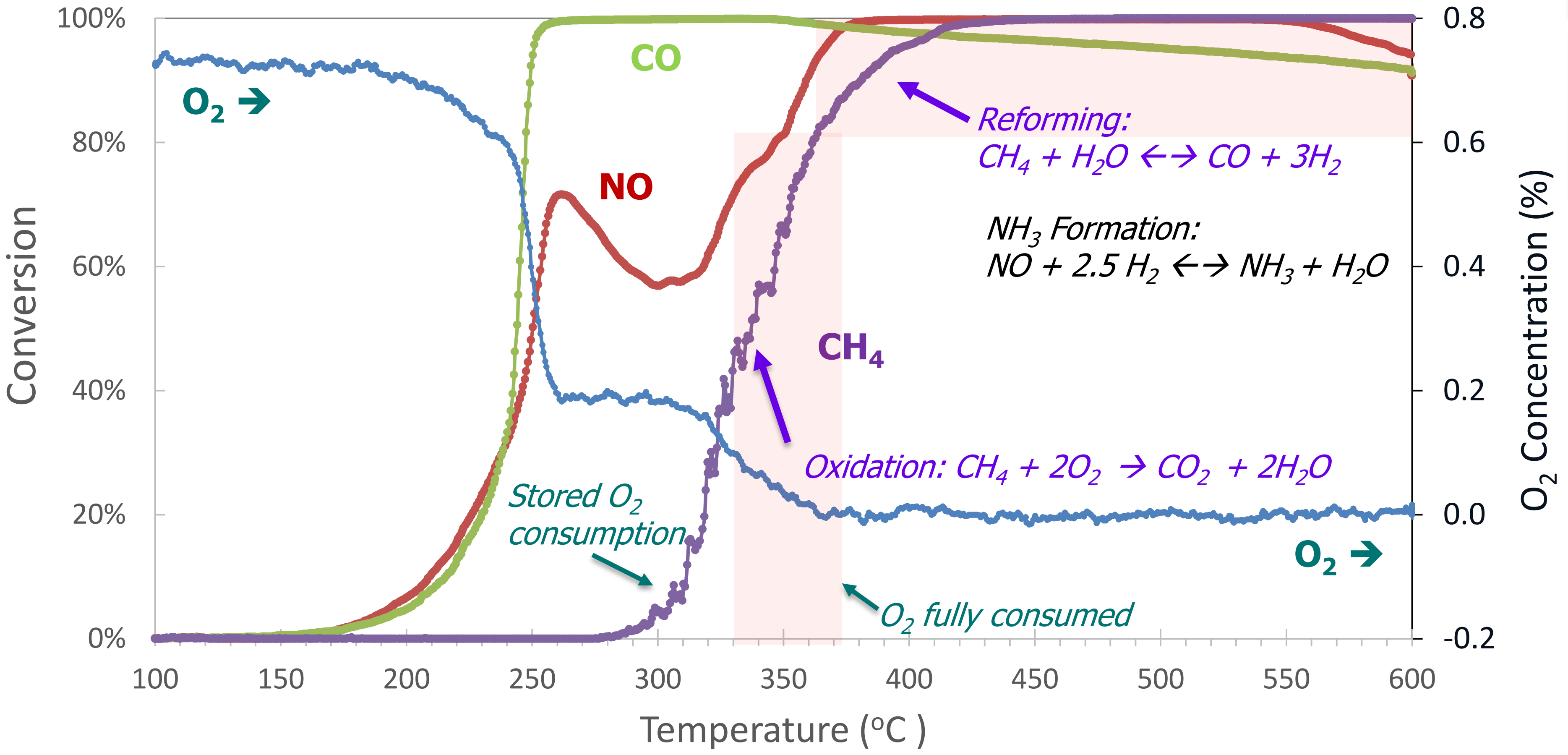
Substrate

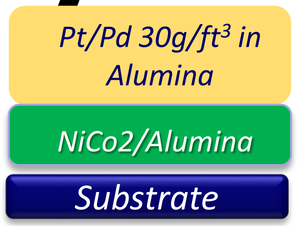
GHSV = 90k hr⁻¹
40 ºC/min
<λ> = 0.996
f = 1 Hz



CH_4 Conversion Light-off: $NiCo_2O_4/Al_2O_3$ + Pt+Pd/Al_2O_3 Dual Layer

- Most (~80%) CH_4 conversion by O_2; remainder (20%) by H_2O/CO_2

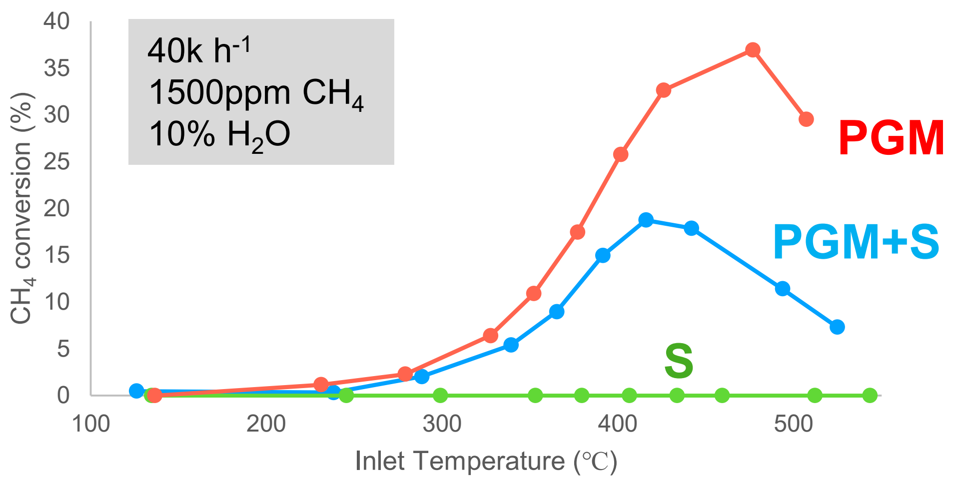




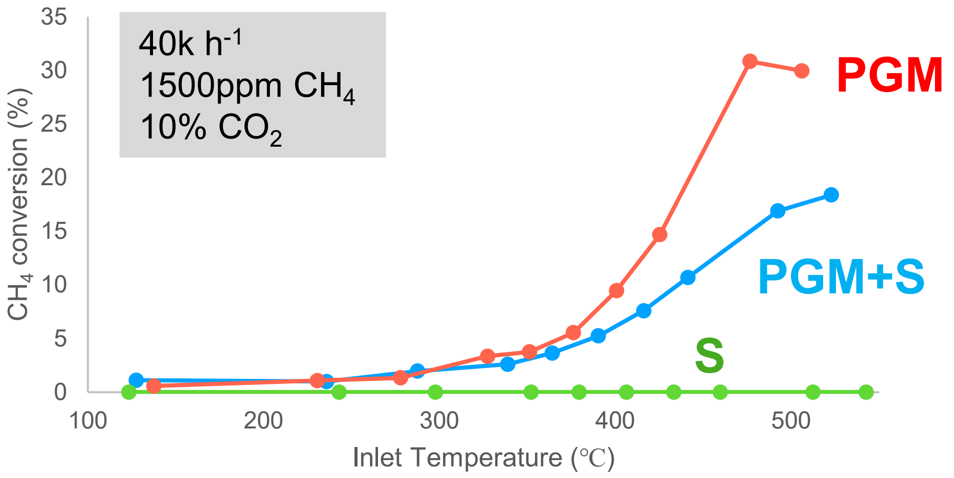
GHSV = 90k hr^{-1}
40 °C/min
<λ> = 0.996
f = 1 Hz
Full feed

Spinel Effect on Reforming Chemistry

Steam reforming

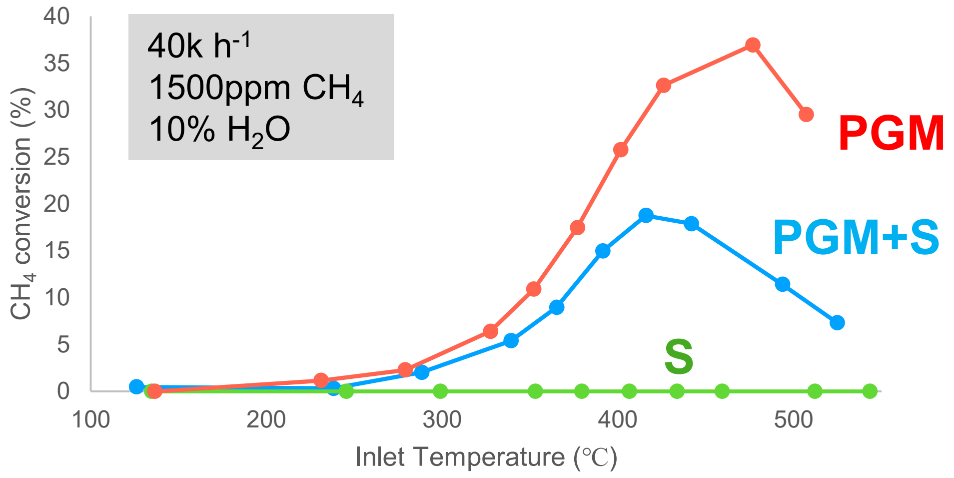


Dry reforming

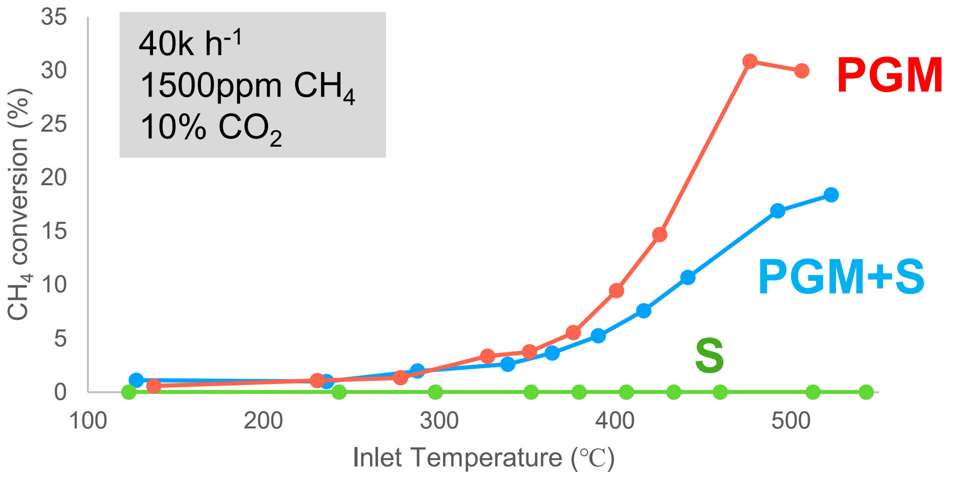


Spinel Effect on Reforming Chemistry

Steam reforming



Dry reforming



- *Spinel not an active component*
- *Spinel addition inhibits reforming activity*
- *Possible factors include:*
  - *Migration of metals (Fe, Mn) to PGM layer*
  - *Enhanced coking*

DOSC Comparison: CH_4 as Reductant

- **"Spinel":**

Al_2O_3-supported Spinel

- **"Metalized Spinel":**

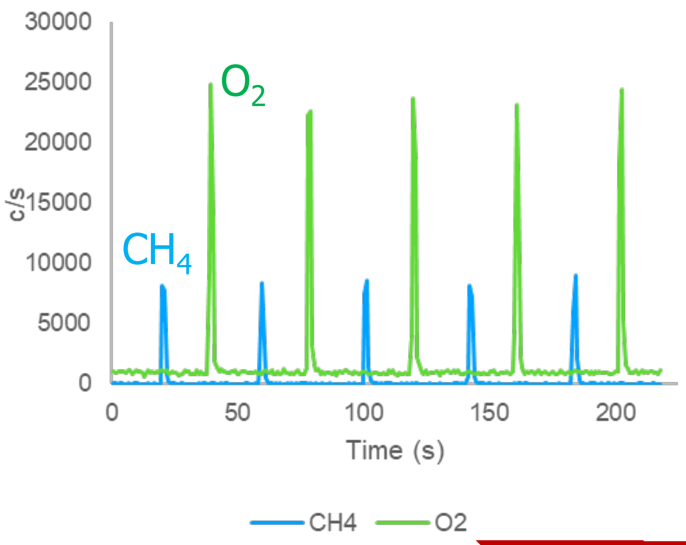
Al_2O_3-supported PGM + Spinel

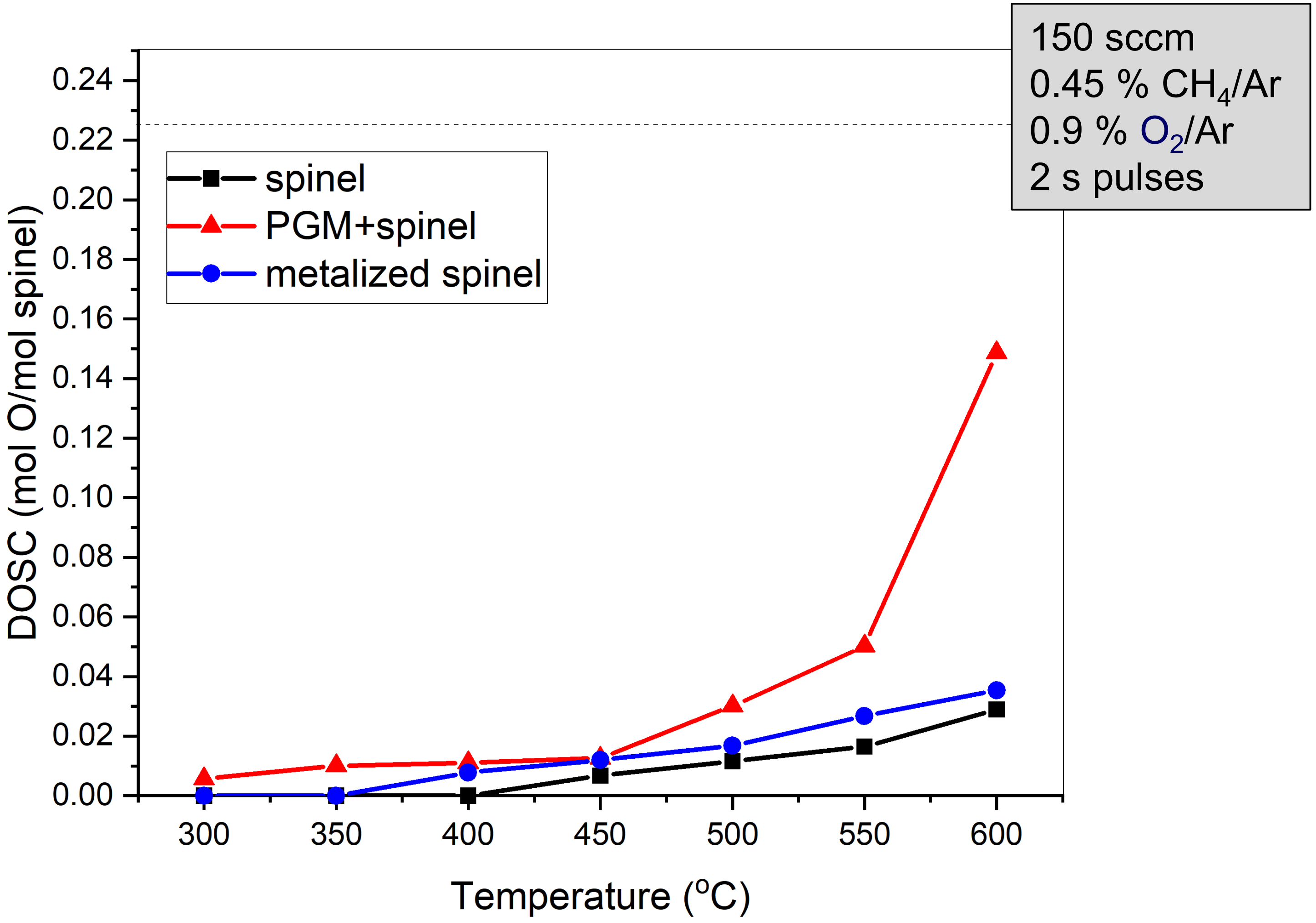
- **"PGM + Spinel":**

PGM/Al_2O_3+ Spinel/Al_2O_3 physical mixture

1 wt% PGM (Pt:Pd = 19:1)

Spinel: 25 wt % $Mn_{0.5}Fe_{2.5}O_4/Al_2O_3$





DOSC Comparison: CH_4 as Reductant

- **"Spinel":**

Al_2O_3-supported Spinel

- **"Metalized Spinel":**

Al_2O_3-supported PGM + Spinel

- **"PGM + Spinel":**

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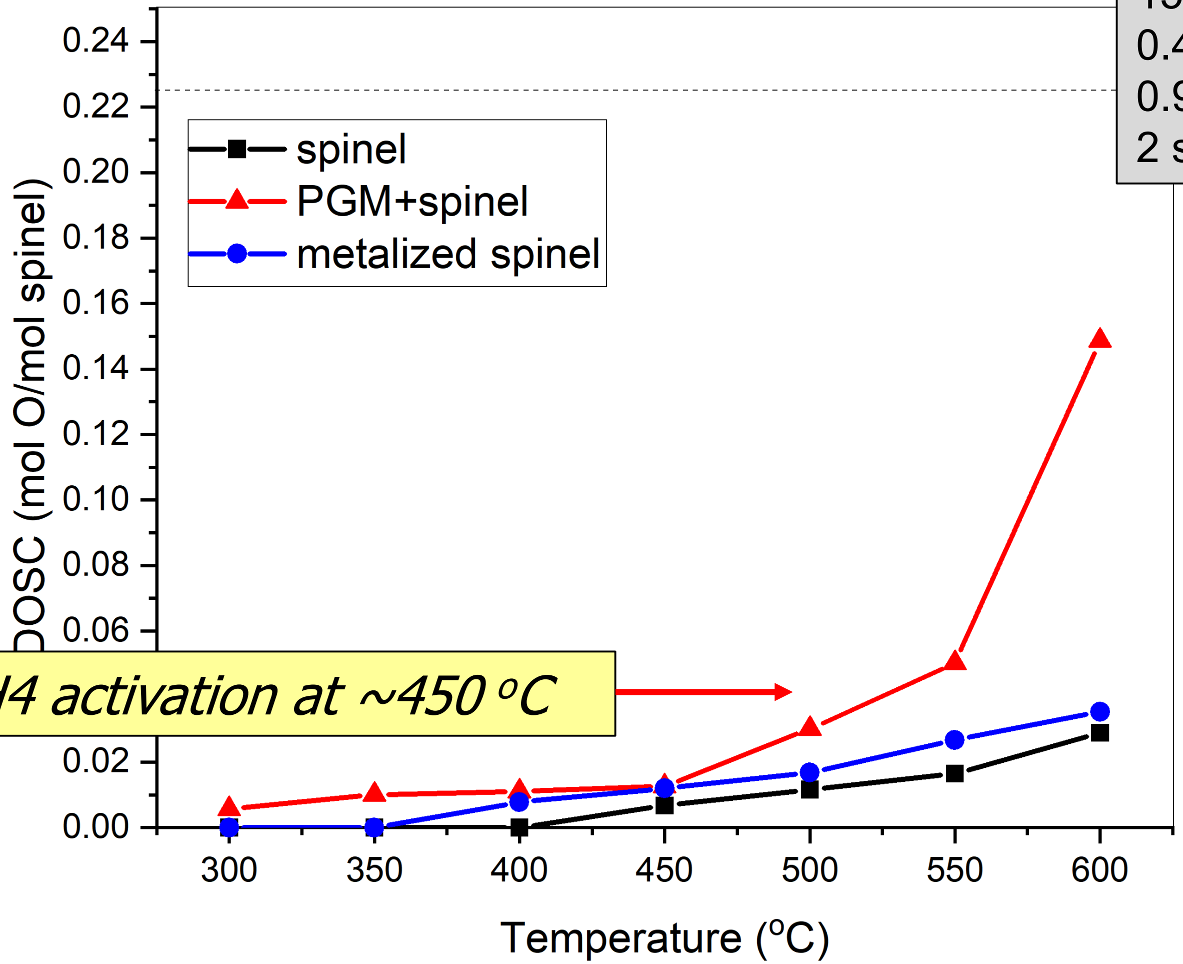
1 wt% PGM (Pt:Pd = 19:1)

Spinel: 25 wt % $Mn_{0.5}Fe_{2.5}O_4/Al_2O_3$

150 sccm
0.45 % CH_4/Ar
0.9 % O_2/Ar
2 s pulses

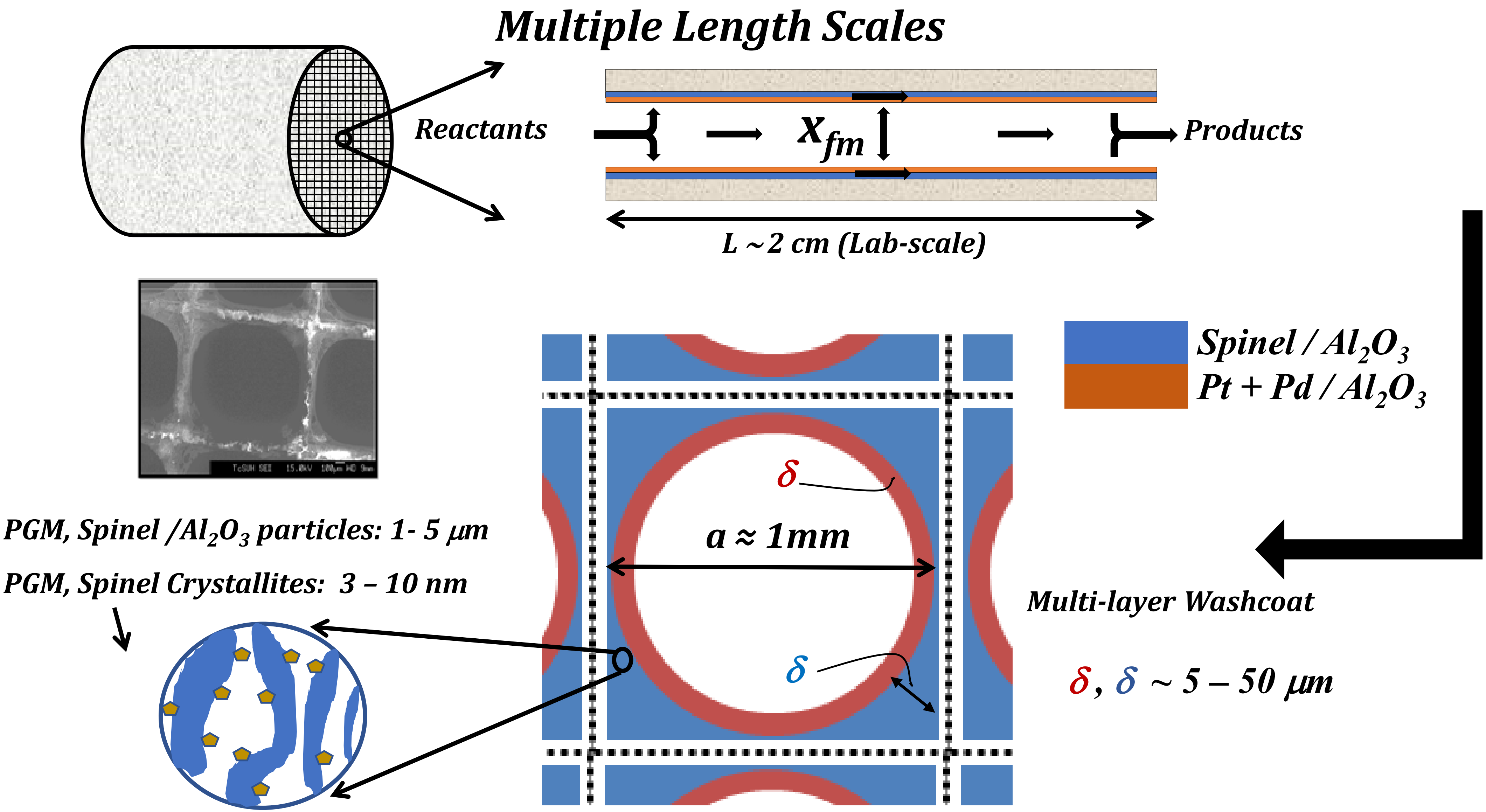


Spinel ($Mn_{0.5}Fe_{2.5}O_4$) promotes PGM CH4 activation at ~450 °C

BP2 Milestones

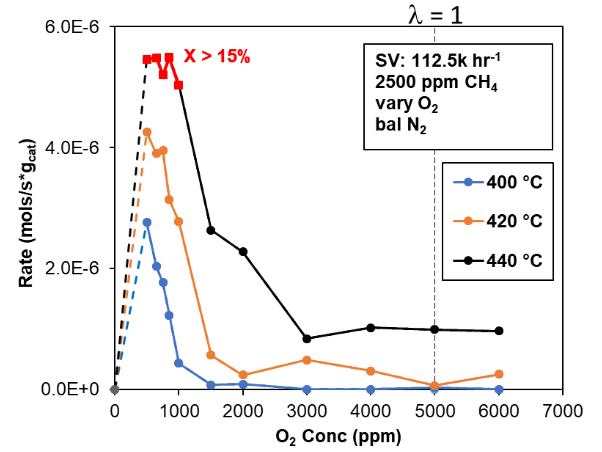
Milestone	Type	Description	Update
Additional Materials Discovery Complete	Technical	Identify at least three additional FWC materials from descriptor-based DFT.	Large number of spinels have been rank-ordered in terms of two descriptors pertaining to methane oxidation activity and oxygen storage capacity.
Materials Synthesis and Screening Complete	Technical	Synthesize and screen performance of materials identified in Task 2.1.	Screening of spinels continues with several candidates identified containing Co, Ni, Mn, and Fe. Experiments underway to quantify dynamic O_2 storage and release of spinels and methane oxidation kinetics.
Stoichiometry modulation Complete	Technical	Complete stoichiometry modulation analysis on Reference and Baseline FWC materials.	Milestone complete for Reference (PGM+Ceria/Zirconia) and Baseline materials.
Monolith Reactor Model Comparison of Baseline and New Materials Complete	Technical	Develop, tune and validate monolith reactor model of new FWC materials and compare to Baseline FWC material.	Development of kinetic model underway for PGM-only; Development of OSM model for CZO & spinel underway;
Rank-Ordering of All Tested Materials Complete	Technical	Rank-order all tested FWC materials in terms of performance with USDRIVE protocol feed.	Database continues to be populated with spinel powders and PGM+spinel monoliths with regards to activity and oxygen storage capacity.
Identification of Candidate Material Complete	Go/No Go	Develop and demonstrate predictive model that predicts performance of Baseline FWC within 15% and which can be used for optimization.	Model framework developed with kinetics studies underway to provide predictive methane oxidation and O_2 storage/release.

Monolith Reactor Model

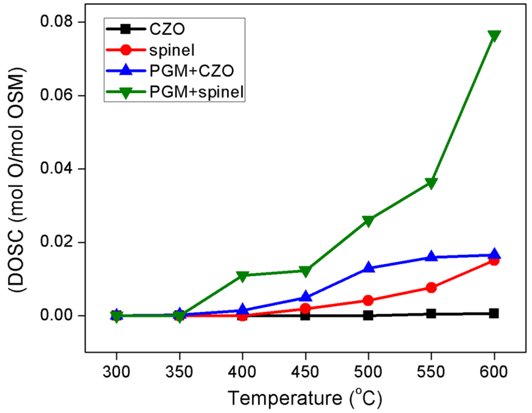


Monolith Reactor Model Elements

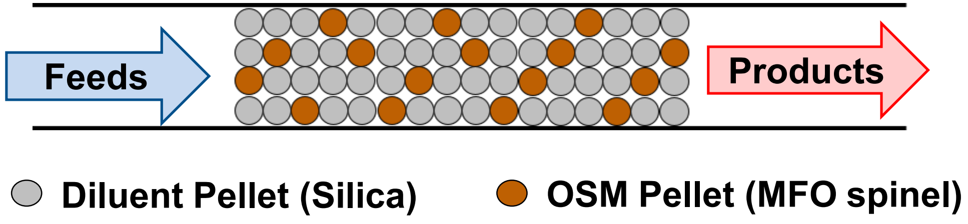
- Pt + Pd $/Al_2O_3$
  - CH_4 oxidation kinetics

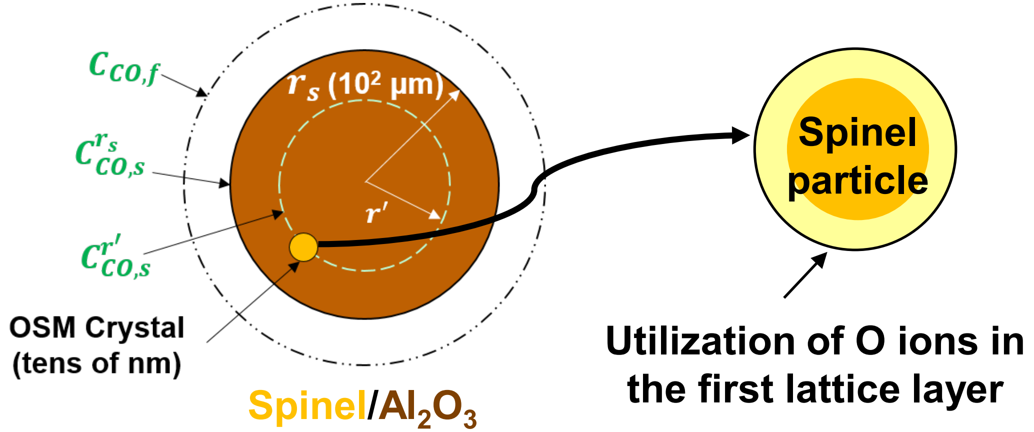


- $Spinel/Al_2O_3$
  - O_2 storage & release kinetics



Spinel O_2 Uptake & Release DOSC Model





- **Species balances in heterogeneous model:**

Fluid Phase	$\frac{\partial x_{f,i}}{\partial t} + \frac{u_f}{\varepsilon_b}\frac{\partial x_{f,i}}{\partial z} = -k_{c,i} a_s \frac{\varepsilon_p}{\varepsilon_b}(x_{f,i} - x_{s,i})$
Solid Phase	$\frac{\partial x_{s,i}}{\partial t} = D_{e,i}\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 \frac{\partial x_{s,i}}{\partial r}) + \frac{1}{C_0}\sum_{j=1}^{r} \upsilon_{nj} r_j$
Site Balance	$\frac{\partial \vartheta_i}{\partial t} = \frac{1}{\Omega_{MFO_4}}\sum_{j=1}^{r} \upsilon_{nj} r_j$

- **Boundary conditions:**

at z = 0	$x_{f,i}(t) = x_{f,i}^{in}(t)$
at r = 0	$\left.\frac{\partial x_{s,i}}{\partial r}\right\vert_{r=0} = 0$
at r =r_s	$k_{c,i}(x_{f,i} - x_{s,i}) = -D_{e,i}\left.\frac{\partial x_{s,i}}{\partial r}\right\vert_{r=r_s}$

- **Reaction Steps**

1) $MFO_4 \underset{O_2}{\overset{CO/H_2}{\rightleftarrows}} MFO_3 + O$

2) $MFO_3 \underset{O_2}{\overset{CO/H_2}{\rightleftarrows}} MFO_{0.5} + 2.5\ O$

MFO_4: $Mn_{0.5}Fe_{2.5}O_4$

- **Rate Expression**

$$r_{1,red.} = k_{1,r} C_{CO} \Omega_{MFO_4} \vartheta_{MFO_4}$$

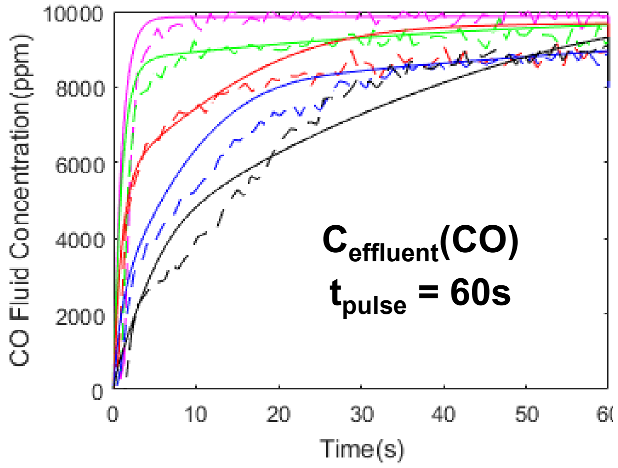
$$r_{1,oxi} = k_{1,o} C_{O_2} \Omega_{MFO_4} \vartheta_{MFO_3}$$

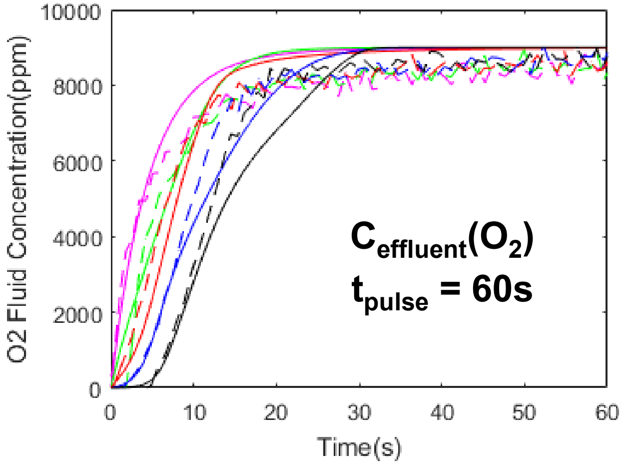
$$r_{2,red.} = k_{2,r} C_{CO} \Omega_{MFO_4} \vartheta_{MFO_3}$$

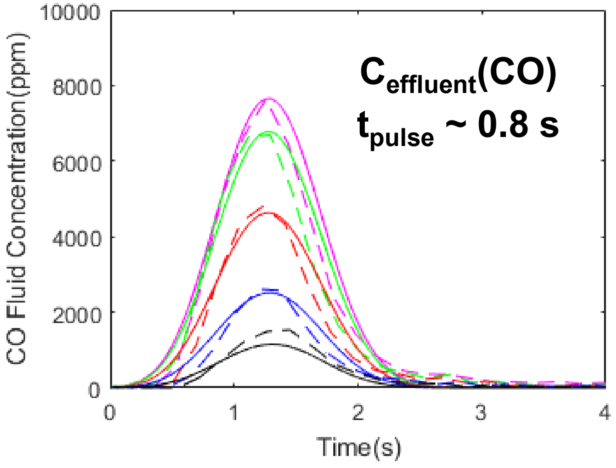
$$r_{2,oxi} = k_{2,o} C_{O_2} \Omega_{MFO_4} \vartheta_{MFO_{0.5}}$$

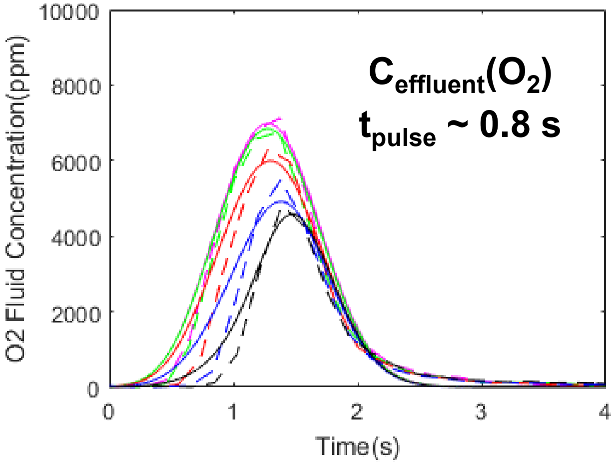
$$\vartheta_{MFO_x} = \frac{N_{MFO_x}}{N_{MFO_4} + N_{MFO_3} + N_{MFO_{0.5}}}$$

DOSC with CO as Reductant: Model vs. Experiment









Experimental Conditions:
1.0% CO/Ar, 0.9% O_2/Ar, <u>60s/ 60s</u>, 15 mg MFO/Al_2O_3, 150 sccm

Experimental Conditions:
1.0% CO/Ar, 0.9% O_2/Ar, <u>0.8s/0.8s</u>, 15 mg MFO/Al_2O_3, 150 sccm

Feed Temperature: **200 C** **300 C** **400 C** **500 C** **600 C**

- - - - : Experimental —— : Modeling

Model predicts long & short-pulse CO-OSC behavior on MFO spinel

Remaining Challenges & Barriers: Defining Future Work

BP3 Milestone	Description
Evaluate different catalyst architectures	Optimize Baseline FWC in terms of layering/zoning.
Sulfur protocol	Develop desulfation protocol for Baseline FWC material.
Converge to final group of FWC materials for engine testing	Document evaluation of Baseline and FWC materials performance with direct comparison using USDRIVE protocol (if available).
Engine testing	Collect NG engine evaluation data for Baseline and new FWC materials.
Converge to best material	Converge to best FWC material based on flow reactor and engine tests.

- Continue to push light-off temperature lower through materials selection & operating strategies, especially for high H_2O concentrations & PGM < 30 g/ft^3
- Evaluate new spinels: $NiCo_2O_4$, Ni_2CoO_4, $NiFe_2O_4$, $CoFe_2O_4$
- Quantify mechanism for conversion enhancement:

  Direct and/or Indirect

  (methane oxidation) (oxygen storage/release)

  - Tools: TAP reactor, DOSC
- Quantify & understand spatial trends during modulation
  - Tool: SpaciMS
- Quantify sulfur tolerance & develop mitigation strategies
- Develop predictive monolith model to guide improvements

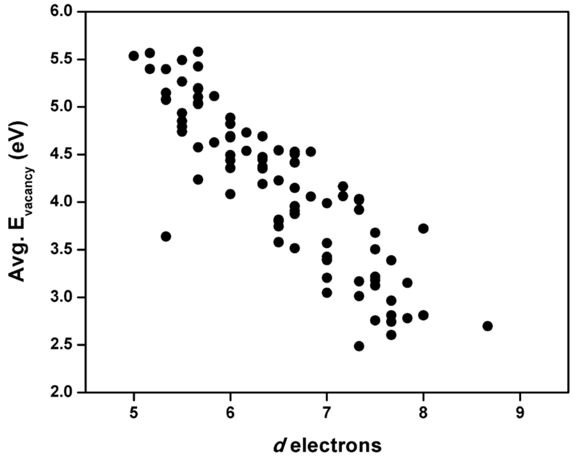
Summary

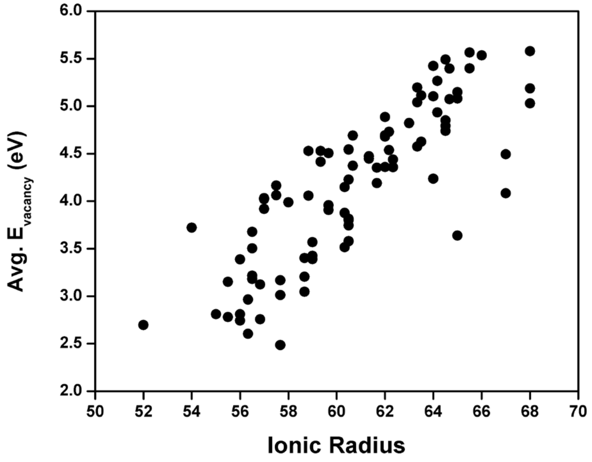
- **Relevance**
  - Enabling emergence of natural gas vehicles by removing emissions hurdle
- **Approach**
  - From molecular-level discovery & mechanism to development & demonstration
- **Technical Accomplishments & Progress**
  - Good progress on all fronts; BP2 milestones achieved
  - New spinels identified through screening
- **Collaborations & Coordination**
  - Cooperation: universities (UH+UVA), national lab (ORNL), industry (CDTi)
- **Proposed Future Research**
  - Converge on next-gen catalysts, integration, modeling, & optimization

Technical Backup Slides

Reducibility-based Rank Ordering of Spinels

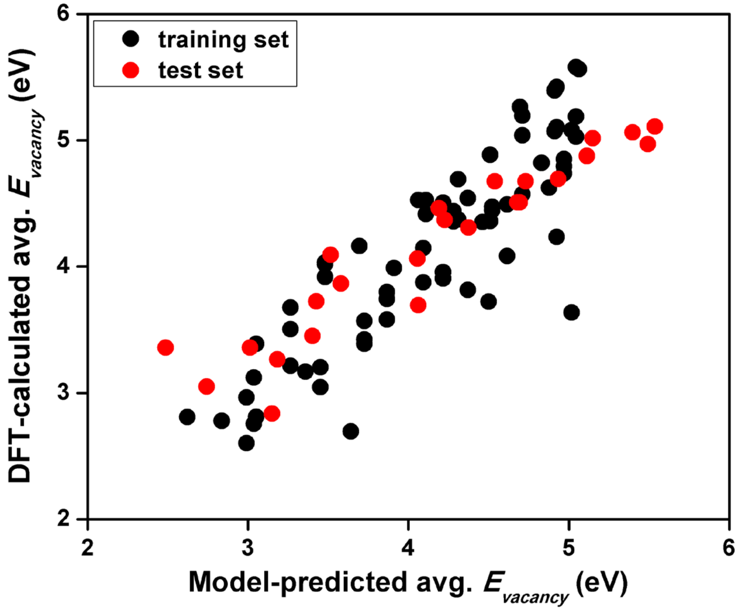
TA1





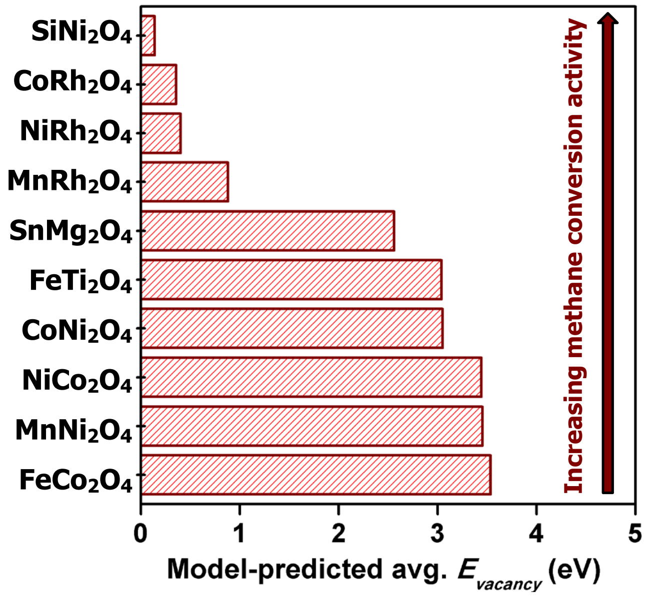
Spinel reducibility as a function of intrinsic material properties

Vacancy formation energy ($E_{vacancy}$) = f(atomic weight, ionization energy, fusion heat, metallic radius)

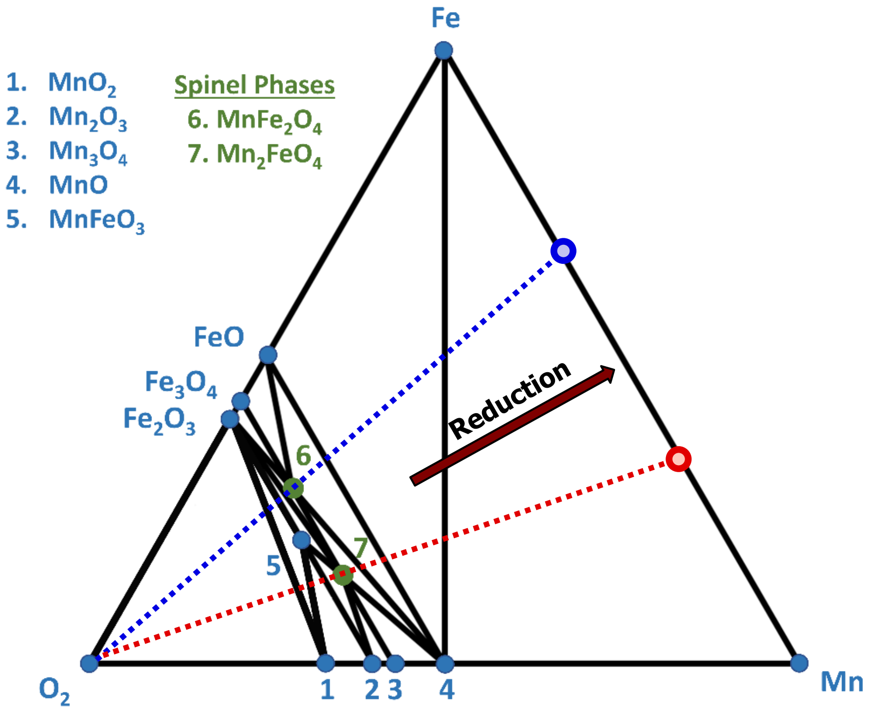


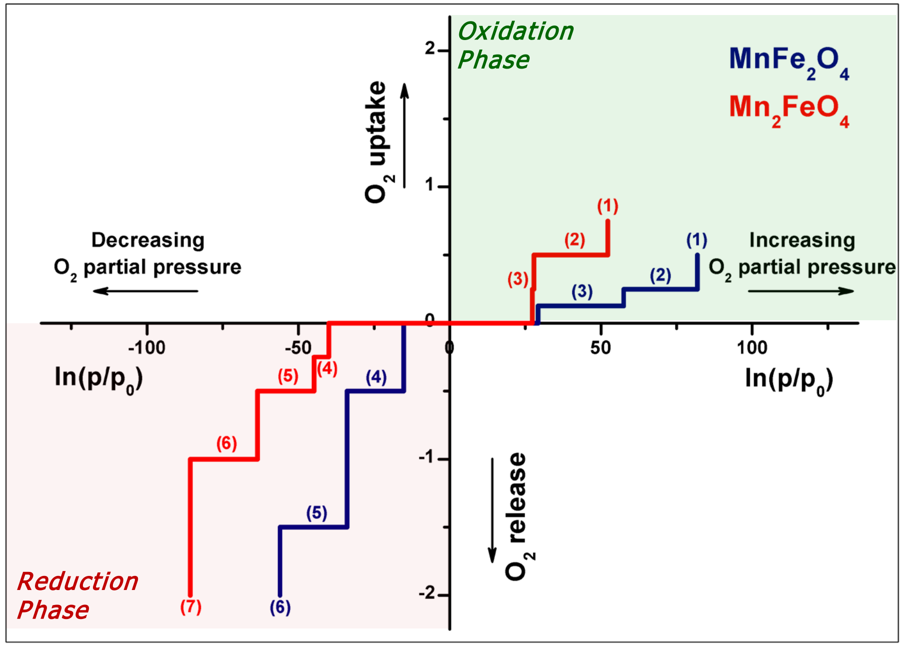
Reducible spinels

(an indication for increased methane activation capability)



Phase Transition Induced DOSC





Phase Transition

from $MnFe_2O_4$ to:

(1) MnO_2, Fe_2O_3
(2) $MnFeO_3$, Fe_2O_3
(3) Mn_2FeO_4, Fe_2O_3
(4) MnO, FeO
(5) MnO, Fe
(6) Mn, Fe

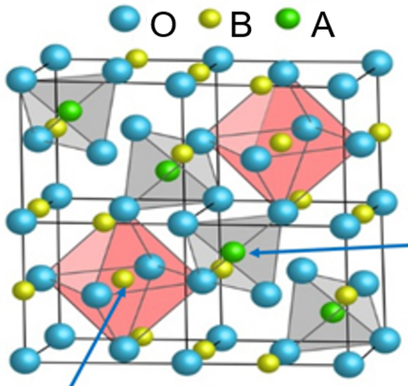
from Mn_2FeO_4 to:

(1) MnO, Fe_2O_3
(2) $MnFeO_3$, MnO_2
(3) $MnFeO_3$, Mn_2O_3
(4) $MnFe_2O_4$, MnO
(5) MnO, FeO
(6) MnO, Fe
(7) Mn, Fe

Steady-state feed over PGM/spinel (10 wt% spinel/alumina), avg. λ = 0.92, 10 °C/min ramp rate

Methane conversion activity (T_{50}) directly correlates with DFT-calculated oxygen vacancy formation energy trends

Dynamic Oxygen Storage Capacity



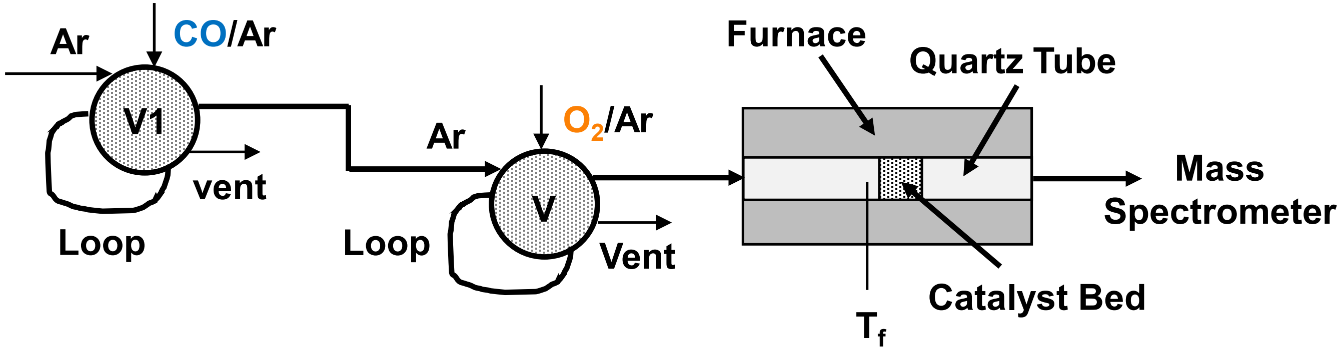
A/B sites: Fe, Mn, Co, Ni, …

A Site – one metal with 4 nearest-neighbor oxygens
Tetrahedral Site

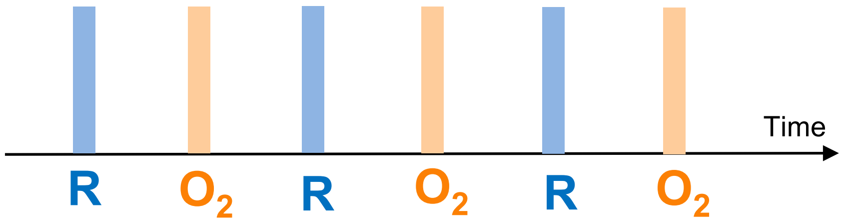
B Site – one metal with 6 nearest-neighbor oxygens
Octahedral Site

Spinel AB_2O_4

$$AB_2O_4 \underset{O_2}{\overset{CO,\ H_2,\ \ldots}{\rightleftharpoons}} AO_x + 2BO_y + z\,O$$

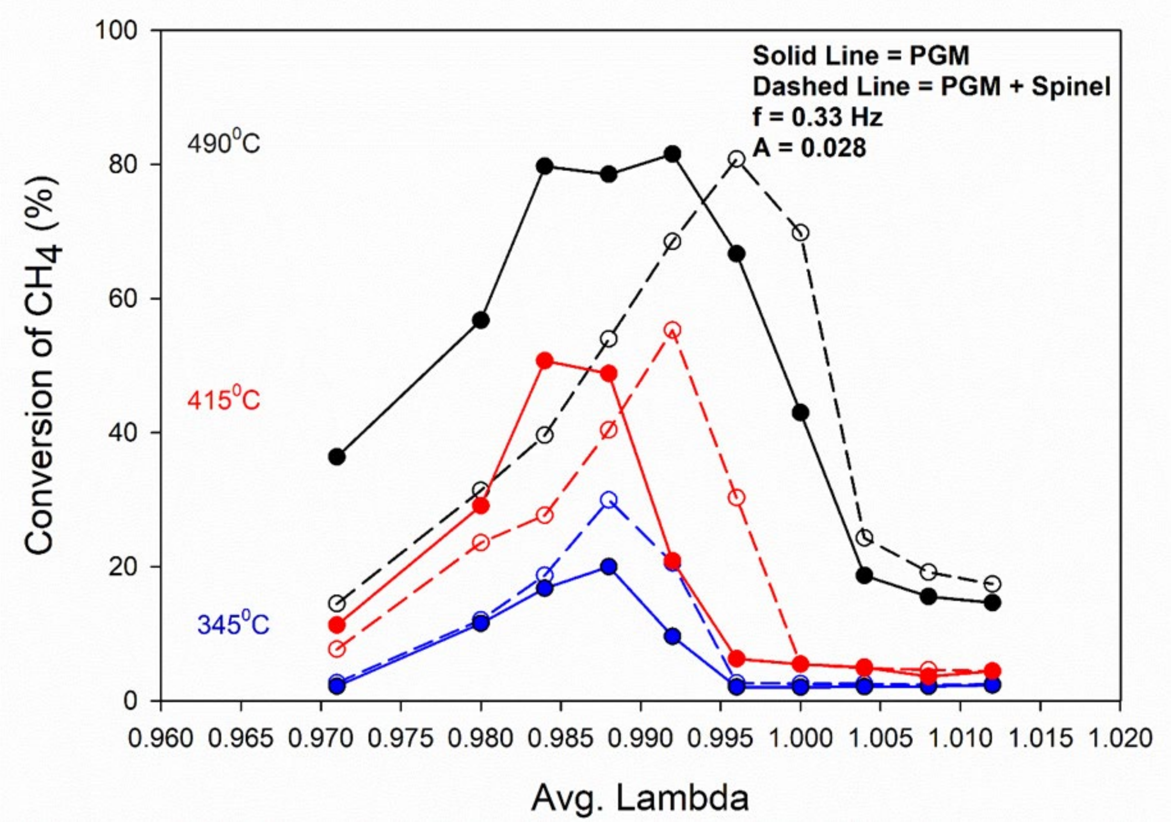


Periodic Pulsing of R (CO, H_2, CH_4) & O_2:



Lambda Sweep: Impact of Spinel Addition

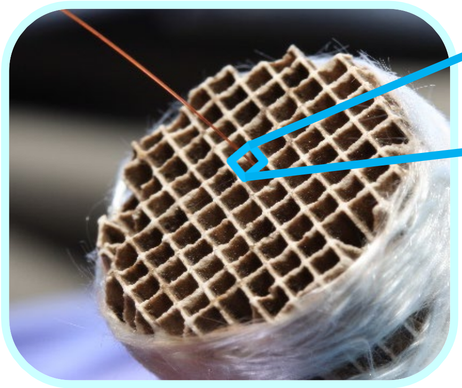
PGM-only (30/0) vs. PGM + Spinel Catalyst (30/100)
(30 g PGM/ft^3; 0 g S/L) (30 g PGM/ft^3; 100 g S/L)

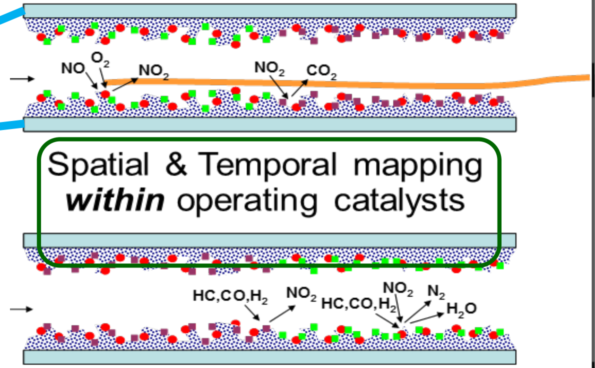


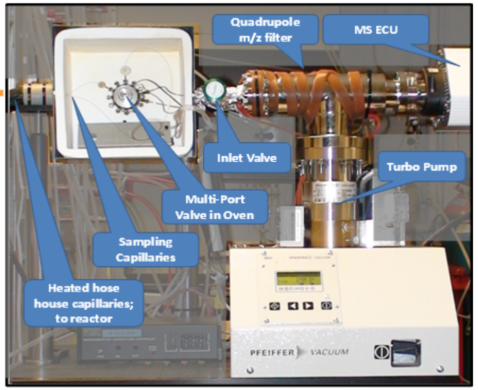
- *Strong O_2 inhibition as $\lambda \rightarrow 1$*
- *Modulation enhancement for both catalysts*
- *Peak conversion moves to $\lambda \rightarrow 1$*

Overview Milestones Relevance Approach **Progress** Future Work Collaborations

Modulation & Spatiotemporal Analysis







Baseline catalyst 30/100; λ = 1.0; Sweep Lambda Amplitude & Frequency